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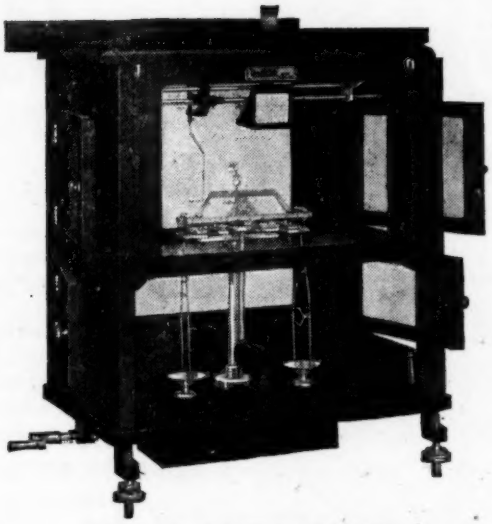

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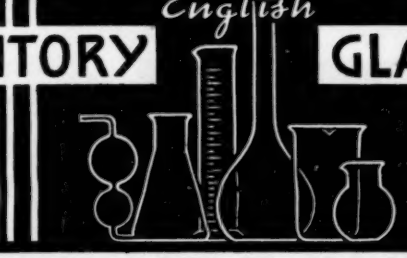

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General, Physical, and Inorganic.

PAGE

4. Rare-earth Metal Amalgams. Part III. The Separation of Ytterbium from its Neighbours.
By JOSEPH K. MARSH 8

14. Some Yttrium-group Oxalates.
By JOSEPH K. MARSH 40

NOTE.—A Rapid Volumetric Method for the Determination of Lead in Brass.
By PHILLIP M. FISK and FRANCIS F. POLLAK 41

Organic.

1. Bromination of Diphenylalkanes and the Preparation of Some Stilbene Derivatives. Part I. αβ-Diphenylethane.
By S. BANCE, H. J. BARBER, and A. M. WOOLMAN 1

2. Taurine.
By ALAN A. GOLDBERG 4

3. The Preparation and Therapeutic Properties of Certain Acridine Derivatives. Part III. 5-Styryl-acridines and their Quaternary Salts.
By W. SHARP, (MISS) M. M. J. SUTHERLAND, and F. J. WILSON 5

5. Synthesis of 4-Hydroxy-2-naphthoic Acids.
By R. D. HAWORTH, BRYNMOR JONES, and YVONNE M. WAY 10

6. The Nuclear Alkylation of Aromatic Bases. Part V. The Action of Methyl Alcohol on *m*-Toluidine Hydrochloride.
By R. W. CRIPPS and D. H. HEY 14

7. β-3 : 4-Methylenedioxyphenyl*iso*propylamine.
By J. ELKS and D. H. HEY 15

8. Physical Properties and Chemical Constitution. Part VII. Alkyl Sulphides, Disulphides, Sulphites, Sulphates, and Orthophosphates.
By ARTHUR I. VOGEL and DAVID M. COWAN 16

9. The Preparation and Polymerisation of Methyl Vinyl Ketone.
By THEODORE WHITE and ROBERT N. HAWARD 25

10. Dinitrodibenzanthrone.
By D. J. BENNETT, R. R. PRITCHARD, and J. L. SIMONSEN 31

11. 1 : 3 : 5 : 7-Tetranitronaphthalene and the Isomeric Tetranitro-derivatives obtained from 2 : 6-Dinitronaphthalene by Nitration.
By JOSEPH CHATT and W. PALMER WYNNE 33

12. The Mechanism of the Oxidation of Oleic and Elaidic Acids and their Methyl Esters by Hydrogen Peroxide in Acetic Acid. Further Observations on the Configurations of the 9 : 10-Dihydroxystearic Acids.
By GEORGE KING 37

13. The Anhydrides of Basic Amino-acids.
By DONALD W. ADAMSON 39

NOTE.—Some Notes on the Condensation Products of Acetaldehyde.
By ERNEST E. CONNOLLY 42

OBITUARY NOTICES 43

INDEX OF AUTHORS' NAMES.

ADAMSON, D. W., 39.
Bance, S., Barber, H. J., and Woolman, A. M., 1.
Barber, H. J. See Bance, S.
Bennett, D. J., Pritchard, R. R., and Simonsen, J. L., 31.
Chatt, J., and Wynne, W. P., 33.
Connolly, E. E., 42.
Cowan, D. M. See Vogel, A. I.
Cripps, R. W., and Hey, D. H., 14.
Elks, J., and Hey, D. H., 15.
Fisk, P. M., and Pollak, F. F., 33, 41.
Goldberg, A. A., 4.
Haward, R. N. See White, T.
Haworth, R. D., Jones, B., and Way, Y. M., 10.
Hey, D. H. See Cripps, R. W., and Elks, J.
Jones, B. See Haworth, R. D.
King, G., 37.
Marsh, J. K., 8, 40.
Pollak, F. F. See Fisk, P. M.
Pritchard, R. R. See Bennett, D. J.
Sharp, W., Sutherland, (Miss) M. M. J., and Wilson, F. J., 5.
Simonsen, J. L. See Bennett, D. J.
Sutherland, (Miss) M. M. J. See Sharp, W.
Vogel, A. I., and Cowan, D. M., 16.
Way, Y. M. See Haworth, R. D.
White, T., and Haward, R. N., 25.
Wilson, F. J. See Sharp, W.
Woolman, A. M. See Bance, S.
Wynne, W. P. See Chatt, J.

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1. *Bromination of Diphenylalkanes and the Preparation of Some Stilbene Derivatives. Part I.* αβ-*Diphenylethane.*

By S. Bance, H. J. Barber, and A. M. Woolman.

The bromination of αβ-diphenylethane to yield 4 : 4′ : α : β-tetrabromo-αβ-diphenylethane is described. This tetrabromo-compound is directly converted by heating with cuprous cyanide in pyridine into 4 : 4′-dicyanostilbene, an intermediate for therapeutically important "Stilbamidine".

4 : 4′-Diamidinostilbene ("Stilbamidine") possesses therapeutic properties (Warrington Yorke *et al.*, *Ann. Trop. Med. Parasit.*, 1940 *et seq.*), and its preparation is therefore important. The manufacturing process devised presents novel features which may be of more general interest.

4 : 4′-Dicyanostilbene has been prepared by Lamb and White (J., 1939, 1256) and by Ashley (J., 1942, 108) from 4 : 4′-diaminostilbene by the Sandmeyer method. This method, however, presented great difficulties on a large scale, giving very poor yields even on a somewhat large laboratory scale.

It would seem preferable, therefore, to synthesise the stilbene molecule from components already containing the nitrile group. A review of published methods (cf. Linnell and Shann, *Quart. J. Pharm.*, 1939, 263), however, makes it evident that most of these cannot be applied satisfactorily with a substituent such as the cyano-group present. For example, although Kuhn and Winterstein (*Helv. Chim. Acta*, 1928, **11**, 103) regard the azine method as the best for preparing stilbene itself, it was not promising, for 4-cyanobenzaldazine had a very high m. p. and did not decompose smoothly at the high temperature required. [Since this work was completed, the preparation of 4 : 4′-dicyanostilbene by repeated sublimation of the azine has been described by Sah (*J. Amer. Chem. Soc.*, 1942, **64**, 1482), but the yield was not good.] 4-Cyanobenzyl chloride, as might be expected, did not yield a Grignard compound, so an attempt by this means to prepare 4 : 4′-dicyanophenylbenzylcarbinol (cf. Ruggli and Lang, *Helv. Chim. Acta*, 1938, **21**, 38) proved abortive. It has already been shown by one of us (J., 1942, 109) that 4-cyanobenzaldehyde under the conditions of the benzoin condensation gives 4 : 4′-dicyanodeoxybenzoin, but the yields are unsatisfactory. Linnell and Shann's attempts (*loc. cit.*) to devise new methods of synthesis did not invite further examination along those lines.

Ruggli's route (*Helv. Chim. Acta*, 1931, **14**, 541) to 2 : 2′-dicyanostilbene through 2-cyanobenzylsulphonyl chloride was not promising, as the yields in converting the sulphonyl chloride with a tertiary base into the stilbene were not good. Condensation of 4-cyanobenzaldehyde with 4-cyanophenylacetic acid would probably yield the desired stilbene, but the number of stages involved in the preparation of each intermediate led us to reject this possibility.

Some experiments on the bromination of αβ-diphenylethane, carried out with another object in view, suggested a new approach to the problem. According to Fittig (*Annalen*, 1866, **137**, 266), bromination of the hydrocarbon under mild conditions yields a mixture of 4-bromo- and 4 : 4′-dibromo-αβ-diphenylethanes, but we have not been able to reproduce these results. Bromination in non-hydroxylic solvents yielded somewhat impure αβ-dibromo-αβ-diphenylethane, m. p. 235°, which according to Wislicenus (*Ber.*, 1895, **28**, 2693) should be regarded as the *meso*-form. If a mixture of bromine and diphenylethane in acetic acid is boiled, however, an easily separable mixture of 4 : 4′ : α : β- and 2 : 4′ : α : β-tetrabromo-αβ-diphenylethanes, $C_6H_4Br{\cdot}CHBr{\cdot}CHBr{\cdot}C_6H_4Br$, is obtained. The former is identical with the product obtained by Wislicenus (*loc. cit.*) by addition of bromine to *trans*-4 : 4′-dibromostilbene. The bromination must involve a simultaneous attack on the aliphatic and the aromatic carbon atoms where substitution takes place, for αβ-dibromo-αβ-diphenylethane is not further brominated under the above conditions, and gradual addition of bromine to a solution of diphenylethane in boiling acetic acid yielded products containing less bromine than is required for the tetrabromo-compound. Bromination of 4 : 4′-dibromodiphenylethane in boiling acetic acid yielded the 4 : 4′ : α : β-tetrabromo-compound.

αβ-Dibromodiphenylethanes can be reduced readily by means of zinc dust to the corresponding stilbene derivatives, but the somewhat large volumes involved made an alternative process desirable. An excellent reducing agent was cuprous chloride or bromide in hot pyridine solution. When these experiments were carried out we were not conversant with the use of pyridine alone for this purpose. According to Pfeiffer (*Ber.*, 1912, **45**, 1810), pyridine eliminates hydrogen bromide from the dibromides having racemic configuration, and bromine from the *meso*-forms. The behaviour of the tetrabromo-compound is in accordance with this, but for smooth decomposition and good yields a considerable excess of pyridine must be used.

The conversion of the dibromo-stilbenes into the dinitriles was readily achieved by heating with cuprous cyanide in pyridine. B.P. 488,642 claims that it is essential to use the theoretical quantity of pyridine, but

we have not found the proportion of pyridine to be of importance within fairly wide limits. These two stages, *viz.*, reduction of the tetrabromo-compound to the dibromostilbene and conversion of this into the dicyanostilbene, have been effected in one operation by using cuprous cyanide instead of the chloride or bromide as the reducing agent, the reaction then becoming $(C_6H_4Br\cdot CHBr\cdot)_2 \xrightarrow{4\ CuCN} (CN\cdot C_6H_4\cdot CH:)_2$. The form in which the halogen is eliminated has not been settled.

If only 2 mols. of cuprous cyanide are used, the product is the dibromostilbene. Moreover, if the tetrabromo-compound is first boiled with pyridine, and 2 mols. of cuprous cyanide are then added, the product is still only the dibromostilbene. The form in which the bromine is combined with the pyridine in this elimination does not appear to have been studied, but it must be fairly reactive. It is hoped to examine these reactions further, and particularly to determine whether the effect of a cuprous salt on the racemic form of the dibromide is to eliminate hydrogen bromide or bromine.

It seems that the reaction can take place in more than two stages, the reduction of the αβ-bromine atoms being the first, and the successive replacement of the nuclear bromine atoms being the second and third. *4-Bromo-4′-cyanostilbene* has now been isolated in traces from mother-liquors from the crystallisation of considerable quantities of 4 : 4′-dicyanostilbene. We have not isolated the *cis*-compound by this method but its formation is not excluded.

The 2 : 4′-isomer underwent a similar series of reactions and *2 : 4′-dicyanostilbene* was obtained. As this yields only a *mono-amidine* and this class of compound is not likely to prove of practical interest, this series of stilbene derivatives was not explored further. The orientation was settled by oxidation to a mixture of *o*- and *p*-bromobenzoic acids.

The greater availability of 4 : 4′-dicyanostilbene has made possible the preparation of some further derivatives of this series. This compound readily took up 2 atoms of bromine to give the *dibromo*-compound $(CN\cdot C_6H_4\cdot CHBr\cdot)_2$, and this was readily converted by alcoholic potash into the *monobromostilbene* $CN\cdot C_6H_4\cdot CBr{:}CH\cdot C_6H_4\cdot CN$, which on more drastic treatment yielded *4 : 4′-dicyanotolane*. 4 : 4′ : α : β-Tetrabromodiphenylethane underwent a similar series of reactions, but more drastic conditions were required for removal of the second bromine atom.

According to Campbell and O'Connor (*J. Amer. Chem. Soc.*, **1939**, **61**, 2897), catalytic reduction of acetylene compounds in presence of Raney nickel yields almost exclusively the *cis*-olefins, whereas with a precious-metal catalyst mixtures are encountered, as is well known. The dicyanotolane on reduction in presence of Raney nickel catalyst yielded the required cis-*4 : 4′-dicyanostilbene*, which underwent the normal rearrangement to the *trans*-form in boiling nitrobenzene containing a trace of iodine (cf. Ruggli, *Helv. Chim. Acta*, **1937**, **20**, 39).

New amidines of this series were prepared, notably *4 : 4′-diamidinotolane* (as *dihydrochloride*) and cis-*4 : 4′-diamidinostilbene* corresponding to "Stilbamidine," which is in the *trans*-form. None of these amidines exhibited any very exceptional trypanocidal properties.

Further experimental work in this group is in progress and has been extended to the preparation of higher homologues.

Experimental.

αβ-Dibromo-αβ-diphenylethane.—(*a*) Bromine, in several vols. of carbon tetrachloride, was added slowly to a nearly boiling solution of *αβ*-diphenylethane (10 g.) in carbon tetrachloride (55 c.c.) until the colour of bromine persisted. 18 G. (4 atoms) of bromine were required. 7 G. of solid separated while still hot, and were recrystallised from glacial acetic acid; m. p. 182—225° (decomp.).

(*b*) *αβ*-Diphenylethane (85 g.) and bromine (117 c.c. = 368 g., 10 atoms) were boiled together in carbon tetrachloride (230 c.c.) for 4½ hours. Hydrogen bromide was evolved, and a crystalline solid began to separate after 5 mins. The solid was filtered off hot and washed with light petroleum; yield 130 g. (83%); m. p. 233—237° (decomp.). 5 G., recrystallised from 350 c.c. of glacial acetic acid [0·7 g., insoluble in the boiling solvent, was removed, m. p. 242° (decomp.)], gave 3·3 g. of m. p. 230—235° (Found: Br, 46·8. Calc. for $C_{14}H_{12}Br_2$: Br, 47·0%).

Attempts to brominate αβ-Dibromo-αβ-diphenylethane.—(*a*) A solution of bromine (5 atoms) in nitrobenzene was added slowly to a boiling solution of *αβ*-dibromo-*αβ*-diphenylethane (16·9 g.) in nitrobenzene (30 c.c.). 5·1 G. of solid separated which, after recrystallisation from glacial acetic acid, gave 4·5 g., m. p. 205—208° (Found: Br, 47·6%); this depressed the m. p. of 4 : 4′-dibromostilbene and was probably impure *αβ*-dibromo-compound.

(*b*) *αβ*-Dibromo-*αβ*-diphenylethane, boiled in glacial acetic acid with an excess of bromine for 6 hours, did not evolve hydrogen bromide and was recovered unchanged.

4 : 4′ : α : β-Tetrabromo-αβ-diphenylethane.—A solution of *αβ*-diphenylethane (30 g.) in glacial acetic acid (330 c.c.) and water (16 c.c.) containing bromine (41 c.c. = 131 g., 10 atoms) was refluxed until no more tetrabromo-compound separated (about ½ hour). The latter was removed hot, and washed with glacial acetic acid and then ether; yield 32 g. (39%); m. p. 235—245° (decomp.).

2 : 4′ : α : β-Tetrabromo-αβ-diphenylethane.—The hot glacial acetic acid mother-liquors from the above bromination deposited *2 : 4′ : α : β-tetrabromo-αβ-diphenylethane* on cooling; yield 30 g. (36%); m. p. 170—175° (Found: Br, 64·1. $C_{14}H_{10}Br_4$ requires Br, 64·2%). No pure product was obtained from the tarry liquid produced by dilution of the filtrate with water.

Addition of Bromine to a Boiling Solution of αβ-Diphenylethane in Glacial Acetic Acid.—Bromine (80 c.c. = 225 g., 9·7 atoms) was added gradually (8 mins.) to a boiling solution of *αβ*-diphenylethane (60 g.) in glacial acetic acid (440 c.c.) and water (22 c.c.); solid crystallised after 2 mins. Boiling was continued for 2 hours, and the product was then filtered off from the hot solution. The filtrate after cooling deposited 30 g. of solid, m. p. 160—195°.

Bromination of 4 : 4′-Dibromodiphenylethane.—(a) *In chloroform.* 4 : 4′-Dibromo-*αβ*-diphenylethane (1·7 g.), dissolved in chloroform (10 c.c.), was treated with bromine (1·8 g., 2·2 atoms) and refluxed for 24 hours. Reaction was very slow and much bromine was unused. 0·5 G. of tetrabromo-compound, m. p. 245—247°, separated on cooling.

(b) *In acetic acid.* 4 : 4′-Dibromo-*αβ*-diphenylethane (1·7 g.) in glacial acetic acid (15 c.c.) was refluxed with bromine (4·5 g.) for 2 hours. The product separated rapidly, and was filtered hot and washed with acetic acid; yield 2·06 g. (83%), m. p. 245—247° (decomp.).

4 : 4′-*Dibromostilbene*.—Cuprous chloride (6·3 g.) was mixed with 4 : 4′ : α : β-tetrabromo-αβ-diphenylethane (12·3 g.) and added to pyridine (25 c.c.). The solid mass produced was melted, boiled under reflux for 1 hour, and poured into about 100 c.c. of concentrated hydrochloric acid. The solid, after being separated and washed with concentrated hydrochloric acid and water, consisted of 8·3 g. of grey solid, m. p. 195—205°, which on recrystallisation from glacial acetic acid gave 6·1 g., m. p. 206—210° (yield 72%).

4 : 4′-*Dicyanostilbene*.—Crude 4 : 4′-dibromostilbene (8·2 g. from a similar preparation to the above) was mixed with cuprous cyanide (6·0 g.) and pyridine (6·5 c.c.) and refluxed, the temperature of the metal-bath being raised to 220° and maintained thereat for 1 hour. The molten mixture was poured into warm concentrated hydrochloric acid (about 100 c.c.), from which the solid was filtered off, washed with concentrated hydrochloric acid, and recrystallised from pyridine; yield 3·6 g., m. p. 282—284°.

Treatment of 4 : 4′ : α : β-*Tetrabromo-αβ-diphenylethane with Cuprous Cyanide and Pyridine*.—(a) *With* 4 *mols. of cuprous cyanide*. The tetrabromo-compound (200 g.) was mixed with cuprous cyanide (224 g.) and pyridine (225 c.c.) and refluxed in a bath at 200—210° for 1½ hours. More pyridine (480 c.c.) was then added, and the whole boiled for 5 mins. to effect more complete solution, and poured hot into 1200 c.c. of concentrated hydrochloric acid. The solid was filtered off hot, washed with about 400 c.c. of hot concentrated hydrochloric acid and then with water, and dried at 100°. 95 G. of product were obtained which, after recrystallisation from nitrobenzene, gave 64 g. of almost pure, pale brown 4 : 4′-dicyanostilbene (70% yield), m. p. 275—280°. If the crude material was sublimed before crystallisation, the yield was higher.

(b) *With* 2 *mols. of cuprous cyanide*. A 60% yield of dibromostilbene was obtained, together with 20% of other, unidentified material. No dicyanostilbene was isolated.

(c) *With* 2 *mols. of cuprous cyanide after boiling in pyridine*. The tetrabromo-compound was boiled for 1 hour in pyridine, 2 mols. of cuprous cyanide were then added, and the mixture heated at 200—210° for a further 1½ hours. There was a considerable evolution of gas which may have contained cyanogen, hydrogen cyanide, and cyanogen bromide. From the reaction mixture a 30% yield of dibromostilbene was obtained but no other product was identified.

2 : 4′-*Dibromostilbene*.—2 : 4′ : α : β-Tetrabromo-αβ-diphenylethane (270 g.) was refluxed for 1½ hours with cuprous chloride (130 g.) dissolved in pyridine (600 c.c.). The mixture was poured into hydrochloric acid (1200 c.c., *d* 1·16), and the product extracted with ether. The crude *dibromostilbene* obtained after removal of ether was distilled in a vacuum, b. p. 185—185°/2 mm., and the distillate recrystallised from alcohol; m. p. 84—85°; yield 116 g., 63% (Found : C, 49·8; H, 3·2. $C_{14}H_{10}Br_2$ requires C, 49·7; H, 3·0%).

Oxidation. The above dibromo-compound (2 g.), dissolved in acetone (10 c.c.), was treated with potassium permanganate (10% solution in 80% acetone) until a permanent excess persisted. After 1½ hours the manganese dioxide was removed, and the solution evaporated to dryness. The residue was dissolved in sodium hydroxide solution and shaken with ether to remove non-acidic material. The mixed acids obtained on acidification had m. p. 220—245°. The *o*-bromobenzoic acid present was converted by boiling with sodium acetate containing a trace of cupric acetate into salicylic acid (cf. Hurtley, J., 1929, 1870), the presence of which was shown by the ferric chloride colour reaction, by conversion into methyl salicylate, and by isolation of a slightly impure salicylic acid (m. p. 149—152°; lit. 159°). *p*-Bromobenzoic acid was also separated in a slightly impure form, m. p. 246—247° (lit. 251°).

2 : 4′-*Dicyanostilbene* was obtained from the corresponding tetrabromo-compound in the same manner as the 4 : 4′-isomer. It was isolated by treating the crude product with hydrochloric acid, extracting it with benzene, filtering off insoluble residue, and evaporating the extract. The residual crude dinitrile was purified by vacuum sublimation or distillation. It formed flat prisms from glacial acetic acid, m. p. 136—137° (Found : C, 83·5; H, 4·3; N, 12·2. $C_{16}H_{10}N_2$ requires C, 83·5; H, 4·4; N, 12·2%).

αβ-*Dibromo*-4 : 4′-*dicyano-αβ-diphenylethane*.—4 : 4′-Dicyanostilbene (9·2 g.) was dissolved in nitrobenzene (50 c.c.) at 200°, and a solution of bromine (2 c.c.) in nitrobenzene (20 c.c.) run in below the surface during 5 mins. in a bright light. Absorption of bromine was rapid, and only traces of hydrogen bromide were liberated. The *product*, which crystallised on cooling, was washed with a little nitrobenzene and ether; yield 12·4 g. (80%), m. p. 269° (decomp.) (Found : N, 7·35; Br, 41·0. $C_{16}H_{10}N_2Br_2$ requires N, 7·2; Br, 41·0%).

4 : 4′ : α-*Tribromostilbene*.—4 : 4′ : α : β-Tetrabromo-αβ-diphenylethane (5 g.), finely powdered, was suspended in boiling ethyl alcohol (100 c.c.), and a solution of potassium hydroxide (1·2 g.) in methyl alcohol (10 c.c.) run in during 10 mins. with vigorous stirring. After a further 10 mins. the solution was filtered from potassium bromide and a little unchanged tetrabromo-compound, diluted with water (10 c.c.), treated with charcoal (0·2 g.), filtered, and diluted to give 70% alcohol. The *product* crystallised in slender prisms (2·8 g.; 70%), m. p. 82—83°. After recrystallisation from methyl alcohol, the m. p. was unaltered but was not sharp, probably owing to the presence of the stereoisomer (Found : Br, 57·6. $C_{14}H_9Br_3$ requires Br, 57·55%).

α-*Bromo*-4 : 4′-*dicyanostilbene*.—αβ-Dibromo-4 : 4′-dicyanodiphenylethane (19·6 g.) was suspended in boiling methyl alcohol (100 c.c.), and 10% methyl-alcoholic potash (30 c.c.) run in during 4 mins. The solution was filtered from unchanged material (4·8 g.) and poured into water. The gum which separated hardened slowly and a solid was separated by trituration with methyl alcohol. The *product* was obtained pure, m. p. 144—145° (Found : C, 62·4; H, 2·3. $C_{16}H_9N_2Br$ requires C, 62·1; H, 2·9%), in small yield after repeated crystallisation from methyl alcohol. The m. p. changed on heating, and the substance was probably contaminated with the *trans*-form. If melted, super-cooled, and then remelted, it had m. p. 130—132°.

4 : 4′-*Dicyanotolane* was obtained from the preceding monobromostilbene but was best prepared directly from 4 : 4′-dicyano-αβ-dibromo-αβ-diphenylethane. This (50 g.) was suspended in a mixture of ethyl alcohol (640 c.c.) and 10% methyl-alcoholic potash and refluxed for 2 hours; the solid was then collected hot, washed with a little hot alcohol and with water, and dried in the oven. The product (18·85 g.) was recrystallised from glacial acetic acid (550 c.c.); yield 16·7 (64·5%), m. p. 252—255°. The alcoholic liquors deposited a further 5·85 g. of the crude product on cooling (Found : N, 12·0; C, 84·4; H, 3·5. $C_{16}H_8N_2$ requires N, 12·3; C, 84·2; H, 3·5%).

4-*Bromo*-4′-*cyanostilbene*.—Residues from mother-liquors of crystallisations of 4 : 4′-dicyanostilbene (kindly supplied by Mr. J. F. Grove, of these laboratories) were sublimed at 250°/1 mm. The product had m. p. 180—220°. Extraction with benzene gave a more soluble fraction which, on fractional crystallisation from glacial acetic acid, gave colourless prisms, m. p. 187—188° (Found : Br, 27·9; N, 5·3. $C_{15}H_{10}NBr$ requires Br, 28·1; N, 4·9%).

2-*Cyano*-4-*amidinostilbene* was obtained in the usual way. On basifying a solution of the hydrochloride, it formed fine prisms, m. p. 200—205° (decomp.) (Found : N, 16·5. $C_{16}H_{13}N_3$ requires N, 17·1%). Attempts to obtain the diamidine by the sodamide method (B.P. 538,463) failed.

4 : 4′-*Diamidinotolane dihydrochloride* was obtained in the usual way from the dinitrile through the iminoether. It formed a hemihydrate (Found : N, 16·1; loss at 100°/2 mm., 3·0. $C_{16}H_{14}N_4,2HCl,\frac{1}{2}H_2O$ requires N, 16·3; H_2O, 2·6%).

cis-4 : 4′-*Dicyanostilbene*.—4 : 4′-Dicyanotolane (34 g.) was suspended in dioxan (350 c.c.), 3·5 g. of Raney nickel catalyst added, and the suspension shaken in hydrogen (30 atm.) for 23 mins. at 60°. The uptake was 1·2 g.-mols. After separation of the catalyst and standing, a small amount of unchanged material separated. This was removed, and the solution concentrated under reduced pressure. On cooling, the cis-*stilbene* crystallised in heavy prisms, m. p.

152—154°; yield 30 g. (87·5%) (Found: N, 12·0. $C_{16}H_{10}N_2$ requires N, 12·2%). On boiling in nitrobenzene solution with a trace of iodine for a few minutes, it was converted into the *trans*-compound, m. p. 278—280·5°.

cis-4 : 4′-*Diamidinostilbene*.—This was prepared in the usual manner from the dinitrile through the iminoether. The solution of the amidine hydrochloride was treated with dilute sulphuric acid to remove some *trans*-4 : 4′-diamidinostilbene as its sparingly soluble sulphate. The *trans*-compound may have been formed in the preparation of the iminoether or its conversion into amidine, or it may have been derived from a small quantity of the *trans*-isomer present in the original *cis*-stilbene dinitrile. The base was obtained as an almost white crystalline solid on adding 50% sodium hydroxide solution to an aqueous solution of the hydrochloride; it was a *monohydrate*, m. p. 204—206° (decomp.) (Found: N, 19·75; loss, 4·35. $C_{16}H_{16}N_4,H_2O$ requires N, 19·8; H_2O, 6·4%).

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Research Division, May & Baker, Ltd., Dagenham. [*Received, October 16th*, 1942.]

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2. *Taurine.*

By Alan A. Goldberg.

A new synthesis of taurine is described together with some sodium acylamidoethanesulphonates.

Taurine has been prepared by Gabriel (*Ber.*, 1888, **21**, 2667; 1899, **22**, 1152), Knorr and Rossler (*Ber.*, 1903, **36**, 1281), and in better yields by Ward (*J. Amer. Chem. Soc.*, 1935, **57**, 914) and Cortese (*ibid.*, 1936, **58**, 191); see also Rumpf (*Bull. Soc. chim.*, 1938, **5**, 877).

It has now been found that β-aminoethyl hydrogen sulphate (easily and rapidly obtained from ethanolamine) reacts smoothly with aqueous sodium sulphite with production of taurine and sodium sulphate. The replacement of halogens by the sulphonic acid group effected by heating alkyl halides with aqueous sodium hydrogen sulphite is well known, but it is remarkable that an alkyl sulphate undergoes a similar reaction in which the carbon–oxygen link in the latter is ruptured and a carbon–sulphur link established. The reaction may be compared with the formation of ethylthiol by the interaction of sodium ethyl sulphate with potassium hydrogen sulphide in aqueous solution (Klason, *Ber.*, 1887, **20**, 3411). At the boiling point under atmospheric pressure (105—108°) the reaction between aminoethyl hydrogen sulphate and sodium sulphite requires *ca.* 30 hours for completion, but under pressure at about 140° reaction is complete in *ca.* 15 hours. The taurine is separated from inorganic salts by means of its high solubility in concentrated hydrochloric acid.

N-Acyl derivatives of taurine in the form of their alkali-metal salts may be readily obtained by the interaction of the acyl chloride with aqueous taurine in the presence of the alkali hydroxide. These compounds, which may be regarded as ethylamides of the acylating acid bearing a sulphonic radical in the ethylamido-group, are extremely soluble in water and highly resistant towards hydrolysis by mineral acids or alkalis. Long-chain acylated taurines in the form of their sodium salts have been used as wetting, emulsifying, and detergent agents which function in liquors of all pH values (B.P. 389,543). Since bacteriostatic aromatic acids such as benzoic and phenylacetic acids, when administered orally or parenterally, undergo detoxication in the liver and kidney by conjugation with natural aminocarboxylic acids (usually glycine), it was of interest to examine the *in vivo* activity of some aromatic acylated taurines in which the acylating aromatic acid is conjugated with a natural amino-sulphonic acid. The sodium salts of the *phenylacetyl*, *phenylpropionyl*, and *acetylmandelyl* derivatives of taurine have been synthesised for examination as urinary disinfectants when administered by the oral and intravenous routes; the pharmacological results will be published separately.

The median lethal dosages (LD_{50}) recorded are for a single subcutaneous injection into 6—8 weeks old white mice weighing 22—24 g.

Experimental.

β-Aminoethyl Hydrogen Sulphate (cf. Fränkel and Cornelius, *Ber.*, 1918, **51**, 1660).—Fuming sulphuric acid (20% SO_3; 100 c.c.) was added (3 hours) with stirring to ethanolamine (50 c.c.) in an ice–salt bath, the temperature never being allowed to exceed 10°. The semi-solid product was kept in the ice-chest overnight, ground with absolute ether (300 c.c.), drained (pump) on sintered glass, dissolved in boiling water (300 c.c.), and quickly filtered (charcoal). The filtrate was poured into rectified spirit (1000 c.c.) and kept for several hours; the aminoethyl hydrogen sulphate separated in lustrous white leaves, which were washed with a small quantity of absolute alcohol and dried in a vacuum. Yield 102 g., 89% (Found: S, 22·6; N, 10·0. Calc. for $C_2H_7O_4NS$: S, 22·7; N, 9·9%).

Taurine: Reaction between Aminoethyl Hydrogen Sulphate and Sodium Sulphite.—(i) *At atmospheric pressure.* A mixture of β-aminoethyl hydrogen sulphate (141 g.; 1 mol.), sodium sulphite heptahydrate (278 g., 1·1 mols.), and water (360 c.c.) was kept boiling (106—108°), in an oil-bath to prevent bumping, for 8 hours on each of two consecutive days. A further quantity of sodium sulphite (139 g.; 0·55 mol.) and water (100 c.c.) was added, the mixture boiled for two further periods of 8 hours, and then evaporated to dryness under reduced pressure. The solid residue was extracted on the water-bath (2 hours) with concentrated hydrochloric acid (1000 c.c.), the extract filtered through sintered glass, and the residue extracted with more concentrated hydrochloric acid (250 c.c.). The combined extracts were cooled, the precipitated sodium chloride removed, and the bulk of the hydrochloric acid distilled off under reduced pressure on the water-bath. Absolute alcohol (500 c.c.) was added to the residual glutinous liquid, crude taurine being precipitated as a white, spongy solid. This was collected, dissolved in the minimum amount of boiling water (200 c.c.), filtered (charcoal), and kept for several hours in the ice-chest, pure taurine crystallising in transparent, colourless needles. These were collected, and dried at 100°/5 mm.; yield 80 g., 63%. They were free from sulphate and chloride ions (Found: S, 25·5; N, 11·3. Calc. for $C_2H_7O_3NS$: S, 25·6; N, 11·2%). From the mother-liquor, which was very rich in taurine, a further quantity of impure taurine (*ca.* 10 g.) was isolated. The sodium sulphate produced during the reaction was found in the form of sulphuric acid in the alcoholic filtrate from the crude precipitated taurine.

(ii) *Under pressure.* A solution of aminoethyl hydrogen sulphate (141 g.; 1 mol.) and anhydrous sodium sulphite (189 g.; 1·5 mols.) in water (700 c.c.) was heated in an autoclave for 20 hours at 140° (50 lb. pressure). The resulting solution was made slightly alkaline with sodium hydroxide, and air bubbled through in order to precipitate any iron. Ferric hydroxide was removed, the solution made just acid with hydrochloric acid and evaporated to dryness, and the residue treated as above described, whereupon pure taurine (78 g.; 62%) was obtained. The solution of a sample in water was free from sulphate and chloride ions (Found: S, 25·6; N, 11·4%). 11 Hours' heating with 1·25 mols. of sodium sulphite, the other conditions being the same as before, afforded only 63 g. (50%) of pure taurine.

Ten parts of taurine dissolve in 17 parts of boiling water and in 50 parts of water at 22°. Median lethal dose 6·0 g./kg.

Sodium Phenylacetamidoethanesulphonate.—Phenylacetyl chloride (15·4 g.) and 5N-sodium hydroxide (20 c.c.) were added during 30 minutes to a stirred, ice-cold solution of taurine (12·5 g.) in 5N-sodium hydroxide (20 c.c.) at such a rate that the pH value of the mixture, as shown by bromothymol-blue and phenolphthalein used as internal indicators, was maintained at 7·6—8·5. Stirring was continued for a further 1½ hours, and the semi-solid product chilled and drained (pump); evaporation of the filtrate gave a second crop of material. The combined solids (26 g.) were recrystallised from the minimum amount of boiling water (40 c.c.), pure *sodium phenylacetamidoethanesulphonate* (19 g.) being obtained in stellate clusters of white leaves (Found, in salt dried at 100°/2 mm. for 1 hour: S, 12·0. $C_{10}H_{12}O_4NSNa$ requires S, 12·1%). Median lethal dose: 8·0 g./kg. (LD50 for phenylacetic acid: 1·7 g./kg.).

Sodium β-Phenylpropionamidoethane sulphonate.—This was obtained in the same manner by adding β-phenylpropionyl chloride (16·8 g.) and 5N-sodium hydroxide (20 c.c.) to a solution of taurine (12·5 g.) in 5N-sodium hydroxide (20 c.c.). Recrystallisation of the crude product from the minimum amount of boiling water (37 c.c.) gave *sodium phenylpropionamidoethanesulphonate* (21 g.) in small white needles (Found in dehydrated salt: S, 11·3. $C_{11}H_{14}O_4NSNa$ requires S, 11·5%). Median lethal dose: 8·0 g./kg. (LD50 for phenylpropionic acid: 1·1 g./kg.).

Sodium Acetylmandelamidoethanesulphonate.—This was obtained in the same manner from acetylmandelyl chloride (21·2 g.) (*Organic Syntheses*, 1941, **21**, 12) and taurine (12·5 g.). The crude product (24 g.) was extremely soluble in water and on evaporation tended to form a "glass"; it was obtained pure by slow crystallisation from dilute methanol in white micro-leaves (Found in dehydrated salt: S, 9·8. $C_{12}H_{14}O_6NSNa$ requires S, 9·95%). Median lethal dose: 8·5 g./kg. (LD50 for acetylmandelic acid: 5·5 g./kg.).

The author thanks Miss M. M. Derrington for assistance with the experimental work, and Dr. F. Scholl for the toxicity figures.

RESEARCH LABORATORIES, WARD BLENKINSOP LTD., BRADFORD-ON-AVON. [*Received, August 26th*, 1942.]

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3. *The Preparation and Therapeutic Properties of Certain Acridine Derivatives. Part III. 5-Styrylacridines and their Quaternary Salts.*

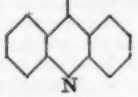
By W. SHARP, (MISS) M. M. J. SUTHERLAND, and F. J. WILSON.

This paper deals chiefly with those 5-styrylacridines containing an amino- or dimethylamino-group in the styryl portion of the molecule, the remainder of the acridine portion being unsubstituted, and their quaternary salts. In some respects the compounds described differ from those given in the literature, as do also some of the reactions. The results of the therapeutic tests will be reported later. The work is being continued.

IN Part II (J., 1938, 654) derivatives of *s*-(6-amino-2-quinolyl)-5-acridylethene and their quaternary salts were investigated. We have now prepared 5-styrylacridines of the type (I, R = NR'R'') and their quaternary salts; their therapeutic properties have been investigated.

By heating 5-methylacridine with *o*-nitrobenzaldehyde there was obtained, instead of the styryl derivative expected, the substance α-(o-*nitrophenyl*)-β-(5-*acridyl*)*ethanol* (II). Attempts to prepare the styryl derivative

(I.)



(II.)

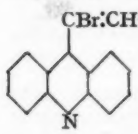
by carrying out the reaction with zinc chloride or acetic anhydride were unsuccessful, nor could the ethanol be dehydrated by acetic anhydride.

Porai-Koschitz, Solodowinkoff, and Troitzki (*Z. Farb.-Ind.*, 1907, **6**, 291) claimed the preparation of 5-m-*nitrostyrylacridine* (I, R = NO_2) by heating 5-methylacridine and *m*-nitrobenzaldehyde with anhydrous zinc chloride. They did not characterise it but converted it into the corresponding amino-compound. Friedländer (*Ber.*, 1905, **38**, 2840), who prepared it by heating the reactants alone, described it as a yellow solid, m. p. 206—208°. On repeating the former experiments, slightly modified, we obtained the nitrostyryl derivative as bright yellow crystals, m. p. 210°. Friedländer's experiment was also repeated, and we obtained the nitrostyryl derivative in small amount as a cream-coloured solid, m. p. 207°, together with a larger amount of α-(m-*nitrophenyl*)-β-(5-*acridyl*)*ethanol* (as II), a pale yellow crystalline solid, m. p. 145°, not described by Friedländer. These two 5-*m*-nitrostyrylacridines, m. p.'s 210° and 207°, gave a depression of m. p. on admixture; the difference may be due to stereoisomerism of the *cis-trans* type. The ethanol could not be dehydrated by heat to give a styryl derivative. For the purposes of this work, we used our preparation of m. p. 210°; on reduction it gave 5-*m*-aminostyrylacridine (I, R = NH_2) with properties as described by Porai-Koschitz *et al.* The *acetyl* derivative (I, R = NHAc), yellow crystals, was converted into 5-m-*aminostyrylacridine methochloride*.

By heating 5-methylacridine and *p*-nitrobenzaldehyde with zinc chloride, Porai-Koschitz *et al.* (*loc. cit.*) obtained 5-*p*-nitrostyrylacridine (I, R = NO_2) as a yellow crystalline monohydrate, becoming anhydrous at 110° and then melting at 212°, analysing both forms. We condensed the two reactants under various conditions

and in no case could this substance be obtained; instead, there resulted the anhydrous nitrostyryl derivative as yellow crystals, m. p. 293°, and showing similar solubility to the substance described by them. Heating the reactants together without zinc chloride gave, in addition to a small amount of the nitrostyryl derivative, m. p. 293°, α-(p-*nitrophenyl*)-β-(5-*acridyl*)*ethanol* (as II) as a pale yellow crystalline powder, m. p. 174°. This ethanol gave, of course, the same analysis as the monohydrated nitrostyryl derivative described by Porai-Koschitz *et al.* but was quite different—it did not lose water on heating at 110° but underwent dehydration on heating with acetic anhydride, yielding our nitrostyryl derivative, m. p. 293°. According to Porai-Koschitz, his nitrostyryl derivative gave on reduction 5-*p*-aminostyrylacridine, m. p. 209°. Our nitrostyryl derivative, m. p. 293°, however, yielded on reduction 5-p-*aminostyrylacridine* (I, R = NH_2) as a yellow crystalline powder, m. p. 242°; again, the difference in these results may be due to stereoisomerism of the *cis-trans* type. This acridine was acetylated, and through the metho-*p*-toluenesulphonate and subsequent hydrolysis with hydrochloric acid was converted into its *methochloride hydrochloride*.

5-*p*-Dimethylaminostyrylacridine (I, R = NMe_2), best prepared by the method of Porai-Koschitz, was converted through the metho-*p*-toluenesulphonate and the methiodide into the *methochloride*.



(III.)

Addition of bromine in chloroform to 5-*p*-nitrostyrylacridine in chloroform precipitated an orange-red *product* considered to be (III), substitution, not addition, having occurred (cf. Loew, *Ber.*, 1903, **36**, 1670, for a similar case).

5-*p*-Aminostyrylacridine dyed wool violet and showed a series of colour changes depending on the pH value of the solution, varying from deep violet to yellow with decreasing pH. *p*-Dimethylaminostyrylacridine also showed a similar series of colour changes from deep blue to yellow, as noted by Porai-Koschitz. Such colour phenomena, which were not shown by 5-*m*-amino- or by 5-*p*-acetamido-styrylacridine, possibly involve a tautomeric quinonoid change of the nature indicated by Porai-Koschitz *et al.* (*loc. cit.*; *Z. Farb.-Ind.*, 1906, **5**, 317). 5-*p*-Aminostyrylacridine methochloride hydrochloride, a reddish-brown crystalline powder, gave a reddish-brown aqueous solution, becoming violet-red on dilution and yellow with a drop of dilute hydrochloric acid; the dilute violet-red solution with ammonia became more violet, and with more ammonia a greenish precipitate slowly formed. The effect of sodium hydroxide was similar; in this respect the methochloride differed from the free amine, which in acid solution on addition of excess alkali gave a yellow precipitate of the free base.

The substances now described have been tested therapeutically; the results, together with others, will be discussed in a subsequent communication. 5-*p*-Aminostyrylacridine methochloride hydrochloride is moderately antiseptic and possesses slight trypanocidal action; the 5-*p*-dimethylamino-analogue is strongly antiseptic but highly toxic. We hope later to report on styrylacridines and their quaternary salts containing substituents in the acridine nucleus.

Experimental.

5-Methylacridine, prepared by Bernthsen's method (*Annalen*, 1884, **224**, 35), was purified through the tartrate (Koenigs, *Ber.*, 1899, **32**, 3607). The *metho*-p-*toluenesulphonate* resulted from heating molecular quantities of the reactants for 2 hours at 145° with occasional stirring. The cold powdered melt could be recrystallised from alcohol with considerable loss and then from alcohol with addition of ether (Found: N, 3·7; S, 8·5. $C_{22}H_{21}O_3NS$ requires N, 3·7; S, 8·5%). The compound, a pale yellow crystalline powder, melted at 204° and was fairly soluble in alcohol, and readily soluble in water to a greenish-yellow solution with intense greenish fluorescence. Addition of ammonia or sodium hydroxide to the solution gave a white precipitate of, presumably, the acridinium base.

5-Methylacridine and o-Nitrobenzaldehyde.—α-(o-*Nitrophenyl*)-β-(5-*acridyl*)*ethanol* (II) was obtained in 81% yield by heating molecular quantities of 5-methylacridine and *o*-nitrobenzaldehyde at 100° for 6 hours, and was recrystallised twice from benzene, forming a pale yellow, crystalline powder, m. p. 177° (Found: C, 73·2; H, 4·7; N, 8·2. $C_{21}H_{16}O_3N_2$ requires C, 73·2; H, 4·7; N, 8·1%); it was sparingly soluble in the usual solvents except pyridine and glacial acetic acid. On attempted reduction with stannous chloride and hydrochloric acid it decomposed into 5-methylacridine. Heating alone at 110° or with acetic anhydride failed to effect dehydration to the styryl derivative, which also was not produced on carrying out the reaction in presence of zinc chloride or acetic anhydride.

5-Methylacridine and m-Nitrobenzaldehyde.—Since the original method of Porai-Koschitz *et al.* gave much tar, the temperature was reduced from 140—150° to 130°. 5 G. of 5-methylacridine and 3·92 g. of *m*-nitrobenzaldehyde were heated with 3·56 g. of anhydrous zinc chloride at 130° for 3 hours. The cold melt, after being powdered, washed with water, and allowed to dry, was recrystallised from pyridine and then alcohol, from which bright yellow crystals of 5-m-*nitrostyrylacridine* (I, R = NO_2), m. p. 210°, separated (Found: C, 77·0; H, 4·4; N, 8·6. $C_{21}H_{14}O_2N_2$ requires C, 77·3; H, 4·3; N, 8·6%); yield 64%. It was insoluble in water and light petroleum, sparingly soluble in hydrochloric acid, ether, acetone, and alcohol. The yellow solution in chloroform gave an orange-red precipitate of a bromo-compound on addition of bromine in this solvent. On carrying out the reaction with acetic anhydride instead of zinc chloride, the same compound resulted in very poor yield.

In absence of a condensing agent, the reaction took a different course. The same amounts of reactants as before were heated at 100° for 7 hours; the brown melt began to solidify after 30 mins. and was quite solid after 45 mins. The powdered product, washed with a little warm alcohol, dried, and then recrystallised three times from benzene, gave a pale yellow crystalline powder of α-(m-*nitrophenyl*)-β-(5-*acridyl*)*ethanol* (II), m. p. 145°; yield 6·76 g. (76%) (Found: C, 73·5; H, 4·8; N, 8·1. $C_{21}H_{16}O_3N_2$ requires C, 73·2; H, 4·7; N, 8·1%). It was sparingly soluble in the common solvents except pyridine and glacial acetic acid. Heating at 110° did not effect elimination of water. The substance decomposed, giving 5-methylacridine, on attempted reduction with stannous chloride and hydrochloric acid.

Evaporation of the benzene mother-liquors from the above experiment left a resinous brown solid, which, after being washed with a little pyridine and then alcohol (washed product = 0·1 g.), was recrystallised from alcohol, from which pale cream crystals of the second form of 5-m-*nitrostyrylacridine* separated (Found: C, 77·8; H, 4·1; N, 8·6%), m. p. 207°. In general solubility it resembled the isomer of m. p. 210°; the mixed m. p. showed a strong depression. The almost colourless chloroform solution gave a reddish precipitate of a bromo-derivative on addition of bromine in this solvent.

5-*m*-Aminostyrylacridine, obtained by reduction of (I, R = NO_2) by the method of Porai-Koschitz (*loc. cit.*) in 91% yield, melted at 234° (lit. 232—234°) and possessed the properties described in the literature. The hydrochloride was

obtained as described by Porai-Koschitz. The *acetyl* derivative crystallised from aqueous alcohol (carbon) in yellow crystals, m. p. 252°; yield 83% (Found: C, 82·0; H, 5·2; N, 8·2. $C_{23}H_{18}ON_2$ requires 81·6; H, 5·3; N, 8·3%); it was insoluble in water, sparingly soluble in ether, benzene, and light petroleum, and soluble in alcohol and chloroform. It resembled the *p*-isomer in turning red with cold dilute hydrochloric acid, in which it was sparingly soluble, but differed from it in giving an orange-yellow solution in glacial acetic acid.

This acetyl derivative was heated with methyl *p*-toluenesulphonate (1 mol.) at 145° for 1 hour with occasional stirring; the powdered product (1 g.) was dissolved in 2 c.c. of water and boiled for 1 hour with an equal volume of concentrated hydrochloric acid. Since no crystals separated on cooling, the solution was evaporated on the water-bath, and the filtered aqueous solution of the yellowish-brown residue was exactly neutralised with potassium carbonate solution. Addition with shaking of solid potassium iodide (1·5 g.) caused immediate precipitation of yellowish-brown 5-*m*-aminostyrylacridine methiodide, which was dissolved in methyl alcohol–water (1 : 1) and boiled for 8 hours with excess of freshly precipitated and washed silver chloride. The solution, after separating and washing residual silver salts with hot aqueous methyl alcohol, left, on evaporation, a yellowish-brown crystalline residue of 5-m-*aminostyrylacridine methochloride*, which was recrystallised from absolute alcohol–ether (Found: N, 8·0; Cl, 10·1. $C_{22}H_{19}N_2Cl$ requires N, 8·1; Cl, 10·3%). It did not melt, but sintered and decomposed above 200° and was slightly hygroscopic; yield 0·3 g. The deep yellow aqueous solution gave no immediate precipitate with a drop of ammonia.

5-Methylacridine and p-*Nitrobenzaldehyde.*—The method of Porai-Koschitz *et al.* (*loc. cit.*) gave only a poor yield of 5-p-*nitrostyrylacridine*, m. p. 293° (cf. p. 6). An improved method was devised, exactly the same conditions being used as for the corresponding *m*-compound; yield 90% (Found: C, 77·6; H, 4·4; N, 8·6. $C_{21}H_{14}O_2N_2$ requires C, 77·3; H, 4·3; N, 8·6%). It formed bright yellow crystals, m. p. 293°, and was not hydrated. In general solubility it agreed with the hydrate of m. p. 212° described by the authors quoted. It developed an orange-red colour with concentrated hydrochloric acid or glacial acetic acid, and an ethereal solution showed a slight greenish-yellow fluorescence. A chloroform solution on addition of bromine in the same solvent gave an orange-red precipitate, which was washed with chloroform and dried. This *product* (III) (Found: Br, 20·2. $C_{21}H_{13}O_2N_2Br$ requires Br, 19·8%) was almost insoluble in the common solvents except pyridine and hot glacial acetic acid; it remained unmelted at 360°.

In absence of zinc chloride the above condensation took a different course. 5 G. of 5-methylacridine and 3·92 g. of *p*-nitrobenzaldehyde were heated at 100° for 6 hours; after 10 mins. a pale yellow solid separated from the brown melt, which then solidified. The powdered product was washed with a little warm alcohol and crystallised twice from benzene; yield 81%. The *α*-(p-*nitrophenyl*)-*β*-(5-*acridyl*)*ethanol* (Found: C, 73·1; H, 4·8; N, 8·1. $C_{21}H_{16}O_3N_2$ requires C, 73·2; H, 4·7; N, 8·1%) was a pale yellow, crystalline powder, m. p. 174°, unchanged by recrystallisation from other solvents or by purification in other ways. It was sparingly soluble in the usual solvents except pyridine and glacial acetic acid, and did not lose water on heating at 110°, in contrast to the hydrate described by Porai-Koschitz, but on heating at 130° with acetic anhydride for 3 hours it yielded the *p*-nitrostyryl derivative of m. p. 293° by elimination of water. On attempted reduction with stannous chloride and hydrochloric acid the compound partly decomposed into 5-methylacridine, isolated as the tartrate, and *p*-nitrobenzaldehyde: even warming with hydrochloric acid brought about this decomposition. In addition to the ethanol, a small amount of the *p*-nitrostyryl derivative was formed as a by-product.

In presence of acetic anhydride, the reaction gave the *p*-nitrostyryl derivative, in alcoholic solution with piperidine the ethanol resulted, but in pyridine solution with piperidine the product was the *p*-nitrostyryl derivative.

5-p-*Aminostyrylacridine* was obtained by reduction of the nitrostyryl derivative by Porai-Koschitz's method, but differed from his product. The stannichloride gave a brown solution in water which became violet on dilution; addition of excess of sodium hydroxide solution to this salt in water gave a yellow-brown precipitate. This precipitate, after being washed with water and allowed to dry, yielded 5-*p*-aminostyrylacridine; recrystallisation from pyridine–alcohol and then washing with alcohol afforded a yellow crystalline powder (Found: C, 85·5; H, 5·5; N, 9·4. $C_{21}H_{16}N_2$ requires C, 85·1; H, 5·4; N, 9·5%); yield 90%. It melted at 242° (Porai-Koschitz, 209°) and was sparingly soluble in alcohol, ether, benzene, and light petroleum, in which solvents Porai-Koschitz's compound is stated to be readily soluble, but was more soluble in pyridine and chloroform. The hydrochloride was obtained in brown crystals by cooling a hot solution of the base in hydrochloric acid. On admixture with bromine, both dissolved in chloroform, a beautiful violet colour developed which on further addition of bromine disappeared with separation of a brown precipitate. The *acetyl* derivative, purified as for the corresponding *m*-compound, was a yellow crystalline powder (yield 82%), m. p. 236° (Found: C, 81·1; H, 5·5; N, 8·3. $C_{23}H_{18}ON_2$ requires C, 81·6; H, 5·3; N, 8·3%), insoluble in water, sparingly soluble in dilute hydrochloric acid (turning red), ether, benzene, and light petroleum, soluble in alcohol, chloroform, acetone, and glacial acetic acid, giving a deep red solution in the last (cf. the free amino-compound, which gave a deep violet). Boiling concentrated hydrochloric acid soon hydrolysed it into the amine. Heating with methyl *p*-toluenesulphonate (1 mol.) at 145° for 1 hour produced the metho-*p*-toluenesulphonate, which when cold was without purification dissolved in water (1 g. per 3 c.c.) and boiled for 1 hour with an equal volume of concentrated hydrochloric acid. After standing overnight, the small, dark reddish-brown crystals of 5-p-*aminostyrylacridine methochloride hydrochloride* (0·5 g.) were collected and washed with a little 15% hydrochloric acid (Found: N, 7·4; Cl, 18·5. $C_{22}H_{19}N_2Cl,HCl$ requires N, 7·3; Cl, 18·5%); further quantities were obtained from the mother-liquors by evaporation, the residue being washed and crystallised from a little alcohol. The salt, a reddish-brown crystalline powder, decomposed with sintering at about 250° and dissolved easily in water to a reddish-brown solution (see p. 6).

5-*p*-Dimethylaminostyrylacridine, prepared in 75% yield by the method of Porai-Koschitz, had properties agreeing with those described in the literature. The hydrochloride, obtained by solution in dilute hydrochloric acid and evaporation on the water-bath, formed dark blue crystals after drying at 100° and gave an intense blue-black solution in water, becoming violet on dilution. The deep red solution of the base in chloroform gave on addition of bromine in this solvent at first a deep violet colour and then a reddish-brown precipitate. The base was heated with methyl *p*-toluenesulphonate (2 mols.) at 145° for 1 hour, and the cooled powdered melt of the crude metho-*p*-toluenesulphonate in a little water was boiled for 1 hour with concentrated hydrochloric acid. On cooling and standing no crystals separated, so the solution was evaporated to dryness on the water-bath, the residue was converted by potassium iodide in the usual way into 5-*p*-dimethylaminostyrylacridine methiodide (yellow-brown, slightly soluble in water, easily soluble in methyl alcohol), and then by means of silver chloride into 5-p-*dimethylaminostyrylacridine methochloride*, which separated in greenish-brown hygroscopic crystals from absolute alcohol–ether (Found: N, 7·5; Cl, 9·5. $C_{24}H_{23}N_2Cl$ requires N, 7·5; Cl, 9·5%). It did not melt but darkened and decomposed above 200° and was easily soluble in water to a deep green solution, which gave no immediate precipitate with a drop of ammonia; yield, 0·45 g. from 1 g. of 5-*p*-dimethylaminostyrylacridine.

We thank the Governors of this College for a Research Assistantship held by one of us (W. S.) for part of the time, and also Imperial Chemical Industries, Limited, for a research grant.

" Freeland " Chemical Laboratories,
The Royal Technical College, Glasgow.

[*Received, October 16th*, 1942.]

4. *Rare-earth Metal Amalgams. Part III. The Separation of Ytterbium from its Neighbours.*

By Joseph K. Marsh.

Lutecium and thulium acetate solutions have no amalgam-forming power when treated with sodium amalgam. Ytterbium acetate forms an amalgam readily and is thus very satisfactorily separated from them, and obtained pure itself. The amalgam is very reactive, and more electropositive than samarium amalgam.

The behaviour of ytterbium acetate on treatment with sodium amalgam differs in several respects from that of samarium acetate (Part II, J., 1942, 523). Ytterbium amalgam is more reactive towards water and air, and less heat is liberated during the reaction $Yb^{\cdots} + 3Na \longrightarrow Yb + 3Na^{\cdot}$ than in that of samarium with sodium, which, however, goes more completely in the above direction. This leads to the view that ytterbium amalgam is more electropositive than samarium amalgam, and approaches more nearly to sodium amalgam, though it is much less stable than the latter. As the reduction takes place in two stages, $E^{\cdots} + Na \longrightarrow E^{\cdot\cdot} + Na^{\cdot}$ and $E^{\cdot\cdot} + 2Na \longrightarrow E + 2Na^{\cdot}$, the stability of the bivalent ion is an important factor in amalgam formation. For ytterbium this stability is much greater than for samarium, but is more than counterbalanced by the reactivity to water of the amalgam itself. The maximum equivalent yields obtained per equivalent of sodium have been 75% for ytterbium and 90% for samarium.

The elimination of ytterbium from its neighbours does not follow the same lines as that of samarium from neodymium and gadolinium, because the neighbours of ytterbium are devoid of amalgam-forming power. The fact that gadolinium had slight amalgam-forming power enabled it to act as a vehicle carrying with it into amalgam the last trace of samarium, yet the bulk of gadolinium was left pure as acetate. The balanced reaction between sodium and ytterbium salts and amalgams makes it impossible to remove the last trace of ytterbium from solution by amalgam formation: 0·01% or more always remained in the non-reducing earth. It is also important that sodium amalgam should be used sparingly at high efficiency, *i.e.*, in as alkaline a solution as possible without hydroxide formation occurring. A too liberal use and a vigorous reduction under more acid conditions only results in the accumulation of sodium acetate in solution, and the consequent back reaction. Frequent removal of sodium acetate is important.

By adding samarium acetate and removing samarium as amalgam, nearly all of the small amount of ytterbium which could not be removed directly was removed with the samarium. Lutecium with a ytterbium content of 0·001% has been thus prepared. This compares favourably with Welsbach's preparations of lutecium containing 1·18% of ytterbium used by Hönigschmid and Wittner (*Z. anorg. Chem.*, 1939, **240**, 284) for the latest determination of the atomic weight.

On the other hand, the purification of ytterbium is even simpler than that of samarium because, provided no early or middle members of the rare earth series be present in the crude material, nothing but ytterbium will pass into amalgam, and the fractional decomposition required in the case of samarium amalgam to eliminate the 1% of neighbouring rare earths which enter the samarium amalgam can be omitted. Ytterbium recovered from a mixture in which thulium and lutecium preponderated was spectroscopically free from them, which places a limit of the order of 0·01% of either present. This is in striking contrast to the findings of Jantsch, Skalla, and Grubitsch (*Z. anorg. Chem.*, 1934, **216**, 75) on the reducibility of anhydrous chlorides by hydrogen at 900° in gold vessels, *viz.*, that thulium and lutecium took the fourth and the fifth place after the three earths which form stable dichlorides, while lanthanum took last place. In view of the structure of the thulium atom, dichloride formation would not be surprising, but in the present work no thulium reduction has been observed. The reduction of lutecium cannot be accounted for by the same mechanism as operates for the three easily reducible earths, *viz.*, the fall of a valency electron to the *N*-shell, because in lutecium this shell is complete. The gold–thulium and gold–lutecium alloys have not been analysed qualitatively, and an element of doubt as to their composition must exist unless the absence of ytterbium in them is proved, more especially as the proportion of metal passing into alloy was not above 25% in either case.

The demarcation between the attack of sodium in amalgam by water or acid and the attack of ytterbium, especially if the latter is at a fairly high concentration, is not entirely sharp. As sodium co-precipitates badly with ytterbium oxalate and causes the latter to become partially soluble, special care to eliminate it must be taken. The absence of ammonia or ammonium salts is necessary, for neither oxalate nor hydroxide precipitations are complete in their presence, and serious loss of material may result.

Ytterbium amalgam remains liquid up to higher concentrations than samarium amalgam. It is thus possible to handle larger amounts of the metal with the same quantity of mercury. The great reactivity of the concentrated amalgam, however, sets an upper limit at 1% to the strength which can be handled.

Experimental.

Purification of Ytterbium.—Ytterbium oxide (97%), prepared by three or four precipitations as ytterbous sulphate (Marsh, J., 1937, 1367), was dissolved in acetic acid after several hours on a water-bath, and the acetate crystallised 270 g.). This salt was dissolved in 1·25 times its weight of boiling water and treated hot with sodium amalgam. There was an immediate production of the orange-yellow colour of the ytterbous ion in concentrated solution. At first, in neutral solution hydrogen liberation was abundant, but it soon slackened and the solution became basic. Hydroxide, blackened by dispersed mercury, was formed, and simultaneously the yellow colour faded to green and then disappeared.

Additions of acetic acid were therefore made to keep the solution somewhat yellow and prevent the formation of hydroxide, but the reaction was kept less vigorous than initially with the solution slightly basic (pH 8—9).

125% of the sodium requirement for the reaction $Yb^{\cdots} + 3Na = Yb + 3Na^{\cdot}$ gave a 98% yield of ytterbium as amalgam. The exchange was very ready and developed little heat. With good shaking the reaction was completed in 2 minutes with least loss of the amalgam through attack by water. Hydroxide formation was prevented by adding sufficient acetic acid. Separation of the solution and mercury was then easy. The mercury was run through two lots of water to wash it from acetate. This brought about decomposition of 1—2% of the amalgam. The washed amalgam was treated with the theoretical amount of dilute hydrochloric acid to decompose the excess of sodium in it. The small amount of ytterbium thereby extracted was precipitated with sodium hydroxide. The amalgam was then treated with excess of hydrochloric acid and shaken till calomel formation began. The first extract of ytterbium hydroxide was added to the chloride solution, which was then concentrated to a syrup. From this, any sodium present crystallised out as chloride, which was then filtered off. The ytterbium solution after dilution was precipitated as oxalate, and the latter ignited to oxide.

In one experiment (see following table) ytterbium acetate (107 g.) was dissolved by boiling in 133 ml. of water in a 1 l. flask. 250 Ml. of sodium amalgam (Na, 30 g.; Hg, 333 ml.) were added, with the addition during the reaction (2 mins.) of 3 ml. of acetic acid; the amalgam was then separated and washed. The acetate solution was next treated with acetic acid (3 ml.) and the remaining amalgam (83 ml.), and during the reaction (2 mins.) with more acetic acid (4 ml.). The solution was then diluted (1·5 l.) and precipitated with alkali. The hydroxide was dissolved in the necessary

Purification of Ytterbium (97%).

Input.					Output.		
Earth, g.	Na, g.	HOAc, ml.	H_2O, ml.	Hg, kg.	Yb_2O_3, g.	Earths, g.	Washings, g.
50	30	10	133	4·5	46·68	—	0·77
	2	3·5	10	0·4	0·44	—	—
	2	2·0	10	0·4	0·20	1·50	—
					47·32	1·50	

minimum of acetic acid, and the rare-earth acetate solution thus freed from sodium acetate was treated with sodium (2 g.) in mercury (30 ml.) and acetic acid (3·5 ml.). Some colour developed towards the end of the reaction. The solution was again precipitated as hydroxide, and the process repeated, after which the remaining earths were once more precipitated as hydroxides, but were subsequently dissolved in nitric acid and precipitated as oxalates and ignited.

The main crop of amalgam after treatment with acid and precipitation as oxalate yielded 46·68 g. of ytterbium oxide. The last ytterbium (0·73 g. of oxide) to be extracted by acid was compared by arc spectroscopy (medium quartz spectroscope) with the main bulk. No rare-earth lines other than those of ytterbium were detected in either. The second and third ytterbium oxide crops (0·44 and 0·20 g.) were not pure white. The residue (1·50 g.) was buff and contained all the yttrium earths. No trace of absorption spectrum was found in 25 cm. of 600 g./l. of ytterbium oxide in solution as chloride from the main crop, but the erbium spectrum was visible in 1 cm. of 7·5 g./l. of oxide from the residue. This indicates: erbium, in residue, 16%; in ytterbium, $<0·008$%.

In another experiment 100 g. of 97% ytterbium acetate (= 46·73 g. of oxide) were treated with the theoretical quantity of sodium (22·7 g.) in amalgam. Acetic acid (7 ml.) was required during the reaction, and 34·2 g. of ytterbium oxide, or 73%, were recovered pure. A similar efficiency was obtained in a third experiment using 60 g. of acetate.

Purification of Lutecium.—A number of small bromate fractions which had been recrystallised several thousand times showed thulium absorption bands at the head, and contained varying quantities of ytterbium. Magnetic measurement (for which the author thanks Prof. Sugden) showed 1—2% at the tail. The tail fractions (5·27 g. of oxide) were converted into acetate (11·75 g.). This was dissolved in 15 ml. of boiling water and treated in a tap-funnel with sodium (0·25 g.) in mercury (7 ml.). There was much effervescence and a green colour developed. Four further similar treatments were given, during which 2 ml. of acetic acid were added (see table). A green colour developed each time. The

Purification of Lutecium.

(Sodium was eliminated after each step except that corresponding to the third line.)

Input.					Output.		
Earth, g.	Sm_2O_3, mg.	Na, g.	HOAc, ml.	Hg, kg.	Yb_2O_3, mg.	Sm_2O_3, mg.	Lu_2O_3, g.
5·37	—	5 × 0·25	2	5 × 0·1	108	—	
	—	5 × 0·25	2·5	5 × 0·1	12	—	
	—	0·25	—	0·1	1	—	
	50	2 × 0·14	0·6	2 × 0·05	—	} 150	
	50	4 × 0·14	1·2	4 × 0·05	—		
	50	5 × 0·14	1·5	5 × 0·05	—		
	50	4 × 0·14	1·2	4 × 0·05	—	} 100?	
	50	6 × 0·14	1·8	6 × 0·05	—		
	—	3 × 0·14	0·9	3 × 0·05	—	2·2	5·12

amalgams were then shaken with 2N-hydrochloric acid till calomel formation began. The acid extracts were treated with excess of alkali, and the hydroxide precipitates collected. The fourth and the fifth treatment gave only small yields; the total was 108 mg. of ytterbia. Most of the lutecium acetate crystallised from its solution overnight; the solubility at room temperature is small. The mother-liquor was decanted, diluted, and rendered alkaline. The resulting hydroxide was collected on a toughened filter, transferred to the tap-funnel, and redissolved in the necessary amount (1 ml.) of acetic acid. The lutecium acetate crystals were then added, and the whole brought into solution (20 ml.) at boiling point. Five more extractions each with 0·25 g. of sodium yielded another 12 mg. of ytterbia. The lutecium was then recovered as acetate or hydroxide as before, and again treated in hot acetate solution with 0·25 g. of sodium in mercury. Only a slight yield of ytterbium oxide (1—2 mg.) was obtained. A quantity of samarium acetate (112 mg.) equivalent to 50 mg. of samarium oxide was now added to the lutecium acetate solution, which was then extracted twice by a total of 0·28 g. of sodium in amalgam. Two further lots of samarium acetate were added and nine extractions made. The last gave a very small yield of oxide. The total yields for the last eleven extractions amounted to 150 mg., *i.e.*, to just the amount of samarium oxide so far added. Two more lots of samarium acetate and 13 more extractions were made as shown.

The last three yielded only 2·2 mg. of oxide. This was proved by arc spectroscopy to be samarium oxide with only a trace of ytterbium. Hence, in all, 35 extractions were made. The first 11 yielded 121 mg. of ytterbium oxide. During the next 24, 0·25 g. of samarium oxide was added and then recovered. Finally, 5·12 g. of lutecium oxide were recovered. The arc spectrum of this material showed at most a faint trace of the ytterbium lines at λ 3289, which had not been reduced materially during the last 13 extractions.

60 Mg. of the purified lutecium oxide were dissolved in nitric acid, and ytterbium nitrate added to produce, on precipitation as oxalate and ignition, lutecium oxide samples containing 1, 0·33, 0·1, 0·033, 0·01, and 0·0033% of added ytterbium oxide. At the lowest concentration the ytterbium doublet at λ 3289 was clearly seen in the arc spectrum. The ytterbium lines at λλ 3694 and 3988 were only seen at 0·01% concentration or more. No samarium or thulium sensitive lines could be identified in the original lutecium oxide. The amount of either, therefore, probably did not much exceed 0·01%. The ytterbium content was below 0·0033% and may be estimated at 0·001%.

In another fraction containing lutecium, ytterbium, and thulium acetates (9·8 g.), three extractions each with 0·5 g. of sodium yielded 0·31 g. of ytterbia. After elimination of sodium, two more extractions, each with 0·25 g. of sodium, yielded a further 4 mg. of ytterbia. Eleven more extractions were made during which 0·7 g. of samaria (as acetate) was added and 3·0 g. of sodium were used. The elimination of ytterbium was not so complete as was obtained by using 0·15 g. of samaria and 1·5 g. of sodium in eleven extractions in the previous experiment. When there was only a little to be extracted, the recovered samarium was found spectroscopically to be richest in ytterbium. Its use probably leads to some real increase in purity, because it is more easily removable from solution by amalgam formation than ytterbium. A purer lutecium spectrum results, but on the other hand, more samarium than ytterbium may escape detection in the arc.

Behaviour of Thulium and Cerium.—In an experiment with 24 g. of acetate chiefly lutecium but with perhaps 25% of thulium, successive yields of ytterbium of 890, 140, 50, 18, 6, 6, 0 mg. were obtained on extraction with sodium amalgam. The first crop of ytterbium oxide failed to show the sensitive arc lines of thulium or lutecium. Thulium, like lutecium, is therefore non-reducible. The arc spectrum showed about 0·01% of ytterbium remaining in the acetate. 1 G. of cerous acetate was added and an attempt made to extract the remaining ytterbium along with the cerium. The strongest ytterbium arc lines were found in each of the four cerium oxide samples recovered, but there was thereafter no appreciable decrease observable in the ytterbium content of the lutecium–thulium mixture. It does not therefore appear that cerium can be used as a satisfactory vehicle for the elimination of ytterbium.

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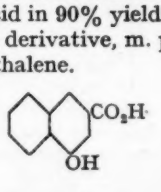
5. *Synthesis of 4-Hydroxy-2-naphthoic Acids.*

By R. D. HAWORTH, BRYNMOR JONES, and YVONNE M. WAY.

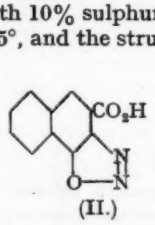
A general method of preparing 4-hydroxy-2-naphthoic acids from benzylsuccinic acids is described. It has been applied to the preparation of 4-hydroxy-, 4-*hydroxy*-6-*methyl*-, 4-*hydroxy*-6-*methoxy*-, 7-*chloro*-4-*hydroxy*-, and 4-hydroxy-1-phenyl-2-naphthoic acids.

THE extensive use of γ-acid and other derivatives of 1-naphtholsulphonic acid as dye intermediate products suggested that derivatives of 4-hydroxy-2-naphthoic acid may have a similar application and the object of the present research was the investigation of methods for the preparation of the acid (I) and its derivatives from benzene compounds.

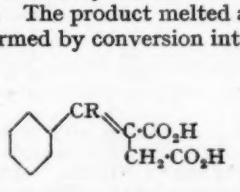
When this work was commenced two independent methods of preparing 4-hydroxy-2-naphthoic acid from naphthalene derivatives were already on record, but their trustworthiness was in some doubt because of the serious discrepancies in the properties reported for the acid and its derivatives. Butler and Royle (J., 1923, **123**, 1653) first reported the conversion of 1-naphthylamine-3-sulphonic acid into (I). The yields were poor (cf. Cason, *J. Amer. Chem. Soc.*, 1941, **63**, 828), and the acid separated from dilute alcohol in small needles, m. p. 182—183°, and gave an acetyl derivative, m. p. 167—168°. Luce, Hofheim, Taunus, and Runne (D.R.-P. 523,358, 1928; *Centr.*, 1931, **2**, 1635) obtained the acid (I) from 4-chloro(or bromo)-3-amino-2-naphthoic acid *via* the diazo-oxide (II) in yellow needles, m. p. 224—225°, giving an acetyl derivative, m. p. 213—214°. While the work in these laboratories was nearing its completion, Cason (*loc. cit.*), presumably without knowledge of the German work, repeated the experiments of Butler and Royle and obtained a small amount of a hydroxy-acid, m. p. 222·5—224·5°. Considerable improvement in yield was effected by distilling sodium 1-naphthylamine-3-sulphonate with potassium cyanide instead of with potassium ferrocyanide, but the outstanding improvement resulted from the observation that 4-amino-2-naphthonitrile was directly converted into 4-hydroxy-2-naphthoic acid in 90% yield by heating with 10% sulphuric acid at 200°. The product melted at 225—226°, gave an acetyl derivative, m. p. 211·5—212·5°, and the structure was confirmed by conversion into 4-hydroxy-2-methylnaphthalene.



(I.)



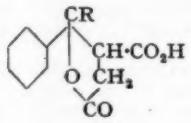
(II.)



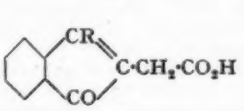
(III.)

The cyclisation of phenylitaconic acids (III) offers in theory the most attractive route for the synthesis of (I) from benzene derivatives, but numerous difficulties are encountered in practice. In the first place, the preparation of these acids from appropriate aromatic aldehydes or ketones and ethyl succinate or succinic anhydride gives, as a rule, very unsatisfactory yields. Numerous by-products such as dibenzylidenesuccinic acids and paraconic acids (IV) are encountered, and references to the earlier work of Stobbe (*Annalen*, 1899, **308**, 90; *Ber.*, 1908, **41**, 4354) illustrate the difficulties which were not surmounted by our preliminary experi-

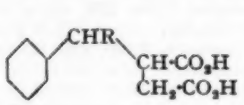
ments. Dehydration of the itaconic acids (III), which presumably precedes their cyclisation with reagents such as concentrated sulphuric acid or aluminium chloride, may occur simultaneously in different ways. The itaconic acids (III) may isomerise to the paraconic acids (IV), which frequently either resist dehydration or require reaction conditions which result in decarboxylation of the product. Dehydration alternatively may lead to the itaconic anhydrides which usually, perhaps invariably, cyclise to indones (V) and not to 4-naphthol-2-carboxylic acids. For example, Stobbe and Vieweg (*Ber.*, 1902, **35**, 1727) showed that diphenylitaconic acid (III; R = Ph) was converted by cold concentrated sulphuric acid into the indone (V; R = Ph). During the course of the present experiments it was observed that phenylmethylitaconic acid (III; R = Me) gave with acetyl chloride an oil which was converted by aluminium chloride in nitrobenzene solution into *4-hydroxy-1-methyl-2-naphthoic acid*, m. p. 205—207°, and a yellow substance, m. p. 125—145°, which has not been purified but is probably the indone (V; R = Me). We are inclined to believe that in this experiment the oil obtained is a mixture containing the anhydride and the paraconic acid (IV; R = Me), which yield the indone (V; R = Me) and the hydroxynaphthoic acid respectively in the presence of aluminium chloride.



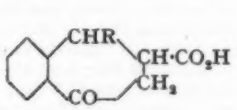
(IV.)



(V.)



(VI.)



(VII.)

The yield of hydroxynaphthoic acid amounts to about 15—20% and the method is of no general preparative interest.

This loss of yield due to indone formation needs to be eliminated, and this can be achieved in two ways. Borsche (*Annalen*, 1936, **526**, 1) showed that the tertiary ester of (III; R = Ph), obtained from benzophenone and ethyl succinate and subsequent partial hydrolysis, was converted by sodium acetate and acetic anhydride into ethyl 4-acetoxy-1-phenyl-2-naphthoate, but this method of avoiding indone formation is neither generally applicable nor does it obviate the objectionable preparation of itaconic acids. Indone formation may be completely eliminated, however, by reducing the itaconic acids to benzylsuccinic acids (VI), the anhydrides of which are readily converted into 1-tetralone-3-carboxylic acids (VII) by the action of aluminium chloride in nitrobenzene (Haworth and Sheldrick, J., 1935, 636). The conversion of the anhydride of diphenylitaconic acid (III; R = Ph) into the indone (V; R = Ph) is probably due to the double bond preventing the approach of that carbonyl group effective in tetralone formation. In the case of the anhydride of the dihydro-derivative (VI) the molecular rigidity is removed and consequently tetralone formation would be facilitated. In view of the difficulty experienced in the preparation of itaconic acids only diphenylmethylsuccinic acid (VI; R = Ph) has been prepared by reducing the corresponding itaconic acid, and other methods for the preparation of acids of type (VI) have been sought.

Ethyl hydroxymethylenesuccinate condenses readily with veratrole, giving high yields of diveratrylsuccinic acid (Haworth and Sheldrick, *loc. cit.*), but the reaction does not occur with benzene, gives only poor yields with anisole, and is not of general application.

The most convenient reaction for the preparation of benzylsuccinic acids depends upon the condensation of an appropriate benzyl chloride with ethyl sodio-α-acetosuccinate to give ethyl α-aceto-α-benzylsuccinates, which were converted into the required benzylsuccinic acids by alkaline hydrolysis. The method has proved suitable for the preparation of benzyl-, *4-methylbenzyl-*, *4-methoxybenzyl-*, and *3-chlorobenzyl-succinic acids*, but experiments with 4-nitrobenzyl chloride and α-methylbenzyl chloride were unsuccessful. The conversions of the benzylsuccinic acids into their anhydrides and subsequently into the 1-tetralone-3-carboxylic acids (VII) presented no difficulties. By the action of bromine in chloroform solution these carboxylic acids were converted into 2-bromo-1-tetralone-3-carboxylic acids, which yielded 4-hydroxy-2-naphthoic acids (I) on warming with diethylaniline. Usually high yields were obtained during the dehalogenation, but decarboxylation with the formation of 1-naphthols occurs to a small extent in some cases. By this method 4-hydroxy-2-naphthoic acid, m. p. 220°, was obtained, and the following substituted hydroxynaphthoic acids have also been prepared: *4-hydroxy-6-methyl-2-naphthoic acid*, m. p. 240—241°, *4-hydroxy-6-methoxy-2-naphthoic acid*, m. p. 238—239°, 4-hydroxy-1-phenyl-2-naphthoic acid, m. p. 205—208° (compare Borsche, *loc. cit.*), and *7-chloro-4-hydroxy-2-naphthoic acid*, m. p. 285—287°. The constitutions assigned to the acids are rigidly established by the method of preparation with the exception of the last-named, and in this case the structure was confirmed by oxidation with alkaline potassium permanganate to 4-chlorophthalic acid.

Of the unsuccessful attempts to develop alternatives routes to the 4-hydroxy-2-naphthoic acids, one only merits mention. *o*-Tolyl methyl ketone, obtained from *o*-toluonitrile and methylmagnesium iodide, condensed readily with ethyl oxalate to form ethyl *o*-toluoylpyruvate, but in spite of the favourable structure, the requisite experimental conditions for its conversion into 4-hydroxy-2-naphthoic acid have not been discovered.

Gattermann and Liebermann (*Annalen*, 1912, **393**, 200) showed that 1-naphthol-3-sulphonic acid reacted with diazo-compounds in positions 2 and 4, coupling in position 4 being favoured by reactive diazo-compounds such as *p*-nitrobenzenediazonium salts. Diazo-compounds couple in alkaline solutions with the various 4-hydroxy-2-naphthoic acids to give red or purplish-red azo-dyes, but the products are amorphous, inseparable mixtures. Definite evidence of coupling in position 1 has been obtained by reducing the crude azo-compound

from 4-hydroxy-2-naphthoic acid and benzenediazonium chloride with hydrogen in the presence of palladium–charcoal, and oxidising the crude aminohydroxynaphthoic acid with ferric chloride to a naphthaquinone-carboxylic acid mixture, which yielded α-naphthaquinone on sublimation. Similar evidence for coupling in position 3 has not been obtained; the ferric chloride oxidation represents a complex reaction which requires further investigation.

Experimental.

Benzylsuccinic Acid.—Benzyl chloride (20 g.) was added to ethyl sodio-α-acetosuccinate (from 30 g. of ester and 3 g. of " molecular " sodium in 100 c.c. of toluene), and the mixture heated for 18 hours in an oil-bath at 120—130°. The cooled mixture was acidified with hydrochloric acid, and the toluene layer separated. The aqueous layer was extracted with ether, the combined toluene and ethereal extracts washed and dried, and the solvents removed. The residue was distilled; the fraction, b. p. 110°/13 mm., containing unchanged reactants was discarded, and the remaining crude ethyl α-aceto-α-benzylsuccinate (30 g.) hydrolysed by boiling with 2N-sodium hydroxide (3 mols.) for 18 hours. Acidification of the cold alkaline solution precipitated benzylsuccinic acid (VI; R = H) as an oil which slowly solidified. The dried solid (16 g.) was dissolved in a small amount of warm acetone, benzene added, and the acetone removed on the steam-bath. The crystals obtained from the cold benzene were recrystallised from water, forming colourless plates, m. p. 157—160° (Fittig and Brooke, *Annalen*, 1899, **305**, 40, give m. p. 161°). Benzylsuccinic anhydride, prepared from the crude acid (14 g.) and cold acetyl chloride, crystallised from benzene–light petroleum (b. p. 60—80°) in plates (11 g.), m. p. 95—97° (Fittig and Roders, *Annalen*, 1890, **256**, 90, 96, record m. p. 102°).

4-Keto-1 : 2 : 3 : 4-tetrahydro-2-naphthoic Acid (VII; R = H).—A solution of anhydrous aluminium chloride (10 g.) in nitrobenzene (35 c.c.) was added to the above anhydride (7 g.), after 24 hours the mixture was decomposed with ice and concentrated hydrochloric acid, and the nitrobenzene removed in steam. The crude product was crystallised from water (charcoal), and the acid (VII; R = H) was obtained in clusters of colourless plates (5 g.), m. p. 145—147° (Derick and Kamm, *J. Amer. Chem. Soc.*, 1916, **38**, 416, give m. p. 143—145°; Attwood, Stevenson, and Thorpe, J., 1923, **123**, 1764, give m. p. 149°).

3-Bromo-4-keto-1 : 2 : 3 : 4-tetrahydro-2-naphthoic Acid.—To a suspension of the finely powdered dry keto-acid (5 g.) in dry chloroform (15 c.c.) a solution of bromine (1·4 c.c.) in chloroform (15 c.c.) was gradually added, and the mixture shaken until the reaction started (10—45 minutes). (It is inadvisable to warm the mixture above about 35° at this stage, since lachrymatory by-products are formed, causing a serious loss of yield.) As the bromination proceeded, a clear, almost colourless solution was obtained, the *bromo*-acid separating later as a fine white deposit, which crystallised from acetone–benzene in colourless prisms (6 g.), m. p. 177—180° (Found: C, 49·6; H, 3·7. $C_{11}H_9O_3Br$ requires C, 49·1; H, 3·4%).

4-Hydroxy-2-naphthoic Acid (I).—The above bromo-acid (6 g.) was heated on the steam-bath with diethylaniline (60 c.c.) for 6 hours. Excess of solid sodium bicarbonate was added to the cold mixture, the diethylaniline removed in steam, and the hot filtered residue cooled and acidified with concentrated hydrochloric acid. The hydroxynaphthoic acid (I) (4·1 g.) crystallised from glacial acetic acid in pale yellow, elongated prisms, m. p. 220—222°. Luce, Hofheim, Taunus, and Runne (*loc. cit.*) record m. p. 224—225°, and Cason (*loc. cit.*) 225—226° (corr.).

4-Methylbenzylsuccinic acid, prepared in 45% yield from 4-methylbenzyl chloride, crystallised from carbon tetrachloride in colourless prisms, m. p. 112—115° (Found: C, 64·8; H, 6·2; equiv., 113. $C_{13}H_{14}O_4$ requires C, 64·9; H, 6·3%; equiv., 111). The *anhydride* crystallised from ligroin (b. p. 90—120°) in colourless plates, m. p. 88·5° (Found: C, 70·9; H, 6·2. $C_{12}H_{12}O_3$ requires C, 70·6; H, 5·9%), and cyclised in the presence of anhydrous aluminium chloride to give a 52% yield of *4-keto-6-methyl-1 : 2 : 3 : 4-tetrahydro-2-naphthoic acid*, which separated from aqueous acetic acid in colourless plates, m. p. 205—207° (Found: C, 70·3; H, 5·8; equiv., 201. $C_{13}H_{12}O_3$ requires C, 70·6; H, 5·9%; equiv., 204). *3-Bromo-4-keto-6-methyl-1 : 2 : 3 : 4-tetrahydro-2-naphthoic acid* crystallised from aqueous acetic acid in colourless elongated prisms, m. p. 167—168° (Found: C, 51·2; H, 3·9. $C_{13}H_{11}O_3Br$ requires C, 50·9; H, 3·9%). Dehalogenation gave an 11% yield of *4-hydroxy-6-methyl-2-naphthoic acid*, which crystallised in pale yellow needles, m. p. 240—241°, from glacial acetic acid (Found: C, 71·4; H, 5·2. $C_{12}H_{10}O_3$ requires C, 71·3; H, 5·0%).

4-Methoxybenzylsuccinic acid, prepared from 4-methoxybenzyl chloride in 20% yield by the hydrolysis of the intermediate ethyl α-aceto-α-(4-methoxybenzyl)succinate, b. p. 175°/0·4 mm., crystallised from benzene in rosettes of colourless plates, m. p. 100—101° (Found: C, 65·3; H, 5·4; equiv., 126. $C_{13}H_{14}O_5$ requires C, 65·5; H, 5·9%; equiv., 119). *4-Methoxybenzylsuccinic anhydride* separated from benzene–light petroleum (b. p. 60—80°) in colourless plates (yield, 92%), m. p. 92—93° (Found: C, 65·3; H, 5·4. $C_{12}H_{12}O_4$ requires C, 65·5; H, 5·5%), and gave *4-keto-6-methoxy-1 : 2 : 3 : 4-tetrahydro-2-naphthoic acid*, which formed colourless plates (yield, 60%), m. p. 151°, from aqueous acetic acid (Found: C, 65·9; H, 5·5. $C_{12}H_{12}O_4$ requires C, 65·5; H, 5·5%). Bromination gave a 70% yield of *3-bromo-4-keto-6-methoxy-1 : 2 : 3 : 4-tetrahydro-2-naphthoic acid*, which crystallised from acetic acid in colourless prisms, m. p. 171° (Found: C, 48·5; H, 3·5. $C_{12}H_{11}O_4Br$ requires C, 48·2; H, 3·7%). This was readily converted into *4-hydroxy-6-methoxy-2-naphthoic acid*, crystallising from acetic acid in pale yellow prisms (yield, 20%), m. p. 238—239° (Found: C, 65·8; H, 4·8. $C_{12}H_{10}O_4$ requires C, 66·1; H, 4·6%).

3-Chlorobenzylsuccinic acid, prepared from 3-chlorobenzyl chloride in 20% yield by hydrolysis of the intermediate ethyl α-aceto-α-(3-chlorobenzyl)succinate, b. p. 180—183°/0·6 mm., crystallised from benzene in colourless prisms, m. p. 125—127° (Found: C, 54·9; H, 4·6; equiv., 128. $C_{11}H_{11}O_4Cl$ requires C, 54·4; H, 4·5%; equiv., 121). The *anhydride* separated from benzene–ligroin in colourless elongated prisms (yield, 85%), m. p. 75·5° (Found: C, 58·3; H, 3·9. $C_{11}H_9O_3Cl$ requires C, 58·8; H, 4·0%), and gave on cyclisation *7-chloro-4-keto-1 : 2 : 3 : 4-tetrahydro-2-naphthoic acid*, which crystallised from acetic acid in colourless plates (yield, 75%), m. p. 190—191° (Found: C, 58·4; H, 4·0; equiv., 224·5). Bromination proceeded smoothly to *7-chloro-3-bromo-4-keto-1 : 2 : 3 : 4-tetrahydro-2-naphthoic acid*, colourless rhombs (yield, 60%), m. p. 180—184°, from acetic acid (Found: C, 43·7; H, 2·6. $C_{11}H_8O_3ClBr$ requires C, 43·5; H, 2·6%). Loss of hydrogen bromide on treatment with diethylaniline gave *7-chloro-4-hydroxy-2-naphthoic acid*, which crystallised from acetic acid in pale yellow, elongated prisms, m. p. 285—287° (Found: C, 59·6; H, 3·4. $C_{11}H_7O_3Cl$ requires C, 59·3; H, 3·2%), and some 6-chloro-1-naphthol as the result of partial decarboxylation. The chloronaphthol, m. p. 90°, gave a picrate which crystallised from aqueous alcohol in orange-yellow elongated prisms, m. p. 163°. Erdmann and Kirchoff (*Annalen*, 1888, **247**, 372) give m. p. 94° for the 6-chloro-1-naphthol and m. p. 165° for the picrate. The orientation of the above chlorohydroxynaphthoic acid was established by oxidation. To a warm solution of the acid (0·5 g.) in an excess of sodium bicarbonate solution a slight excess of N/2-potassium permanganate was added. The mixture was warmed for 5 minutes, and the manganese dioxide removed and washed. The concentrated filtrate and washings were acidified with concentrated hydrochloric acid, a small amount of orange-coloured impurity removed, and the filtrate extracted with ether. The extract was washed with sodium bicarbonate, the acid recovered by acidification, taken up in ether, and dried. Removal of the solvent left an oil which readily solidified on trituration with benzene and melted at 149—150° after crystallisation from acetone–benzene. The m. p. of 4-chlorophthalic acid has been variously reported as 148°, 150° and 150·5° (see Moore, Marrack, and Proud, J., 1921, **119**, 1788).

Methyl 7-chloro-4-hydroxy-2-naphthoate after crystallisation from methyl alcohol and benzene separated from the latter in colourless elongated prisms, m. p. 218—220°, and 7-chloro-4-methoxy-2-naphthoic acid crystallised from ethyl alcohol in rosettes of colourless prisms, m. p. 251—258°.

4-Hydroxy-1-phenyl-2-naphthoic Acid.—4-Keto-1-phenyl-1 : 2 : 3 : 4-tetrahydro-2-naphthoic acid, which crystallised in colourless plates, m. p. 208—209°, from glacial acetic acid, was prepared as described by Hewett (J., 1936, 596). Bromination gave *3-bromo-4-keto-1-phenyl-1 : 2 : 3 : 4-tetrahydro-2-naphthoic acid*, which after two crystallisations from acetone–benzene separated in colourless prisms, m. p. 199—202° (Found : C, 58·8; H, 3·7. $C_{17}H_{13}O_3Br$ requires C, 59·1; H, 3·8%). 4-Hydroxy-1-phenyl-2-naphthoic acid, obtained in 70% yield by dehalogenation with diethylaniline, crystallised from aqueous acetic acid in colourless needles, m. p. 205—208°, undepressed by a sample of the acid prepared by Borsche's method (*loc. cit.*). Some 4-phenyl-1-naphthol, m. p. 136—138° (Borsche, *loc. cit.*, gives m. p. 140°), was isolated from the bicarbonate-insoluble fraction.

4-Hydroxy-1-methyl-2-naphthoic Acid.—Some particulars of this preparation kindly supplied by Imperial Chemical Industries Ltd. were modified, and the following method adopted.

Phenylmethylitaconic acid (III; R = Me) was prepared from acetophenone (7·2 g.), ethyl succinate (19 g.), and sodium ethoxide (8·3 g.) by a method similar to that of Stobbe (*Annalen*, 1899, **308**, 114). The crude acid (9 g.), m. p. 125—140°, probably a mixture of isomers (see Stobbe, *loc. cit.*), was refluxed with freshly distilled acetyl chloride (30 c.c.) for 2—3 hours, and the excess of chloride then removed by distillation under reduced pressure. The oily product (8 g.) was dissolved in nitrobenzene (8 c.c.) and a solution of aluminium chloride (8 g.) in nitrobenzene (30 c.c.), previously cooled in ice, was added. After 48 hours concentrated hydrochloric acid was added, and the nitrobenzene removed in steam. The brown semi-solid was dried and triturated with cold benzene, leaving a bright yellow solid. From this, boiling benzene extracted a yellow material, probably an indone derivative, which crystallised from the benzene and melted at 125—145°, leaving *4-hydroxy-1-methyl-2-naphthoic acid* (4·5 g.) as a pale brown solid which, after repeated crystallisation from glacial acetic acid, gave colourless plates, m. p. 203—207° (Found : C, 71·1; H, 5·0. $C_{12}H_{10}O_3$ requires C, 71·3; H, 5·9%). The naphthoic acid structure (I) was confirmed by conversion into the following derivatives by the use of standard methods. The *methyl* ester crystallised from benzene in rhombic prisms, m. p. 171—174° (Found : C, 72·9; H, 5·5. $C_{13}H_{12}O_3$ requires C, 72·2; H, 5·6%). The *ethyl* ester, crystallised similarly, had m. p. 127—129° (Found : C, 73·2; H, 6·2. $C_{14}H_{14}O_3$ requires C, 73·0; H, 6·1%). The *methyl* ether separated from ligroin (b. p. 90—120°) in clumps of needles, m. p. 158—160° (Found : C, 72·1; H, 5·3. $C_{13}H_{12}O_3$ requires C, 72·2; H, 5·6%), and *methyl 4-methoxy-1-methyl-2-naphthoate* after crystallisation from methyl alcohol was obtained in colourless rhombs, m. p. 99·5° (Found : C, 73·0; H, 6·1. $C_{14}H_{14}O_3$ requires C, 73·0; H, 6·1%).

o-Methylacetophenone.—*o*-Toluonitrile (12 g.) in toluene (30 c.c.) was treated with methylmagnesium iodide (magnesium, 2·4 g.; methyl iodide, 14 g.; ether, 60 c.c.), and the mixture kept overnight. The ether was removed on a water-bath, and the residue boiled for 3 hours. Dilute sulphuric acid was added to the cold mixture, the toluene layer separated, and the aqueous layer extracted with ether. The combined toluene and ethereal extracts were washed and dried, and after the removal of the solvents through a column the residual oil was distilled. The ketone (9 g.) distilled at 93—95°/13 mm. and gave a semicarbazone, m. p. 209° (Mercer, Robertson, and Cahn, J., 1935, 999, give b. p. 93—95°/15 mm. for the ketone and m. p. 210° for the semicarbazone; cf. also Baker, J., 1938, 447).

Ethyl o-Methylbenzoylpyruvate.—A mixture of *o*-methylacetophenone (2 g.) and ethyl oxalate (2·2 g.) was added to an ice-cold solution of sodium (0·34 g.) in dry alcohol (5 c.c.). After 24 hours the sodium salt deposited was collected, dissolved in water, and treated with carbon dioxide. The oil liberated was extracted with ether, washed, and dried, and the solvent removed. The unpurified ethyl *o*-methylbenzoylpyruvate (1 g.) was added to a cold solution of sodium (0·23 g.) in dry alcohol (2·5 c.c.), and after several hours the deposit of sodium salt was collected, dissolved in water, and acidified. The dry solid crystallised from benzene in clusters of pale buff plates, m. p. 118° (Found : C, 64·7; H, 4·9%). It dissolved readily in aqueous sodium bicarbonate and is probably *o*-methylbenzoylpyruvic acid ($C_{11}H_{10}O_4$ requires C, 64·1; H, 4·9%).

The addition of diazotised amines to solutions of the hydroxynaphthoic acids in sodium hydroxide gave the colour reactions tabulated below. An asterisk denotes the formation of a precipitate. In each experiment two drops of a dilute solution of the diazotised amine were added to ten drops of a solution of the hydroxynaphthoic acid containing 0·5 mol. of the acid per litre of N-sodium hydroxide.

2-Naphthoic acid.	Aniline.	*p*-Toluidine.	*p*-Nitro-aniline.	α-Naphthyl-amine.	Benzidine.	Sulphanilic acid.
4-Hydroxy-	Dark cherry-red*	Cherry-red*	Brilliant purplish-red	Cherry-red	Bright crimson	Bright cherry red
4-Hydroxy-6-methyl-	Ruby-red	Dark red	Purple	Purplish-red*	Bluish-purple	Bright red
4-Hydroxy-6-methoxy-	Ruby-red	Dark red	Purplish-red*	Purplish-red*	Purplish-red	Bright red
7-Chloro-4-hydroxy-	Brownish-red*	Bright red*	Purplish-red*	Cherry-red	Purplish-red*	Light red
4-Hydroxy-1-phenyl-	Ruby-red	Bright red*	Purplish-red*	Purplish-red	Deep blue*	Crimson-red
4-Hydroxy-1-methyl-	Ruby-red	Crimson-red	Purplish-red*	Cherry-red	Deep blue*	Bright red

Coupling of Diazotised Aniline with 4-Hydroxy-2-naphthoic Acid.—The diazo-solution, prepared from aniline (0·5 g.), 4% hydrochloric acid (10 c.c.), and 0·32% sodium nitrite solution (12·4 c.c.), was added to 4-hydroxy-2-naphthoic acid (1·0 g.) dissolved in 10·6% sodium hydroxide solution (12 c.c.). After 15 minutes the solution was acidified with concentrated hydrochloric acid and the dark red azo-compound (1·3 g.) was collected, washed, and dried on porous plate. The azo-compound (0·5 g.), which could not be crystallised and was apparently a mixture, was dissolved in absolute alcohol and shaken with hydrogen in the presence of 5% palladium–charcoal (0·2 g.) until absorption ceased (80 c.c.). Filtration and removal of the alcohol in a vacuum left amino-4-hydroxy-2-naphthoic acid as a brown residue. This (0·2 g.) was dissolved in hot dilute hydrochloric acid, filtered, and treated with a solution of anhydrous ferric chloride (0·6 g.) and a few drops of concentrated hydrochloric acid. After 10 minutes the precipitated naphthaquinonecarboxylic acids were collected, washed, and dried. The nitrogen-free precipitate, m. p. 153—160° (decomp.), which was soluble in sodium bicarbonate solution, was slowly sublimed at 1 mm. The bright yellow needles, m. p. 120—123°, which sublimed at 100—140° (bath temperature) were identified as α-naphthaquinone by colour tests and direct comparison with an authentic specimen. The red or orange-red product, m. p. 130—150°, which sublimed at 140—200° could not be purified or identified.

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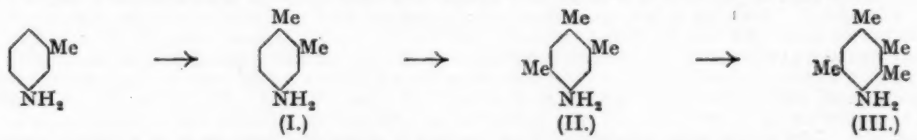
THE UNIVERSITY, SHEFFIELD, 10. [*Received, September 17th*, 1942.]

6. *The Nuclear Alkylation of Aromatic Bases. Part V. The Action of Methyl Alcohol on* m-*Toluidine Hydrochloride.*

By R. W. Cripps and D. H. Hey.

The action of methyl alcohol on *m*-toluidine hydrochloride in equimolecular proportion at 210—235° gives *o*-4-xylidine in 30% yield. With 3 mols. of methyl alcohol, *ψ*-cumidine is obtained in about 50% yield, whereas with 4 mols. at higher temperatures the products are *iso*duridine, *iso*durenol, and pentamethylphenol.

In an earlier communication on the Hofmann–Martius reaction (Hey, J., 1931, 1581) a study was made of the action of methyl alcohol on the hydrochlorides of *o*- and *p*-toluidine at 250—300°. In view of the importance of *o*-4-xylidine as an intermediate in the preparation of riboflavin (vitamin B_2) attention has now been directed to the application of this reaction to *m*-toluidine hydrochloride, which when heated in an autoclave with methyl alcohol should give rise successively to *o*-4-xylidine (I), *ψ*-cumidine (II), and *iso*duridine (III).



Limpach (*Ber.*, 1888, **21**, 643) states briefly that the action of methyl alcohol on *m*-toluidine hydrochloride at 250° gives a primary base identical with *o*-4-xylidine, and a casual mention of the formation of *o*-4-xylidine from *m*-toluidine was also made by Liebermann and Kardos (*Ber.*, 1914, **47**, 1563). Noelting and Forel (*Ber.*, 1885, **18**, 2680) reported the formation of *ψ*-cumidine from *o*-4-xylidine hydrochloride and methyl alcohol at 300—320°. Noelting and Baumann (*ibid.*, p. 1145) reported the formation of *iso*duridine from the action of methyl alcohol on *ψ*-cumidine hydrochloride at 200° and finally at 300°, and stated that the same base was formed in similar manner from mesidine hydrochloride, a claim which was contested by Limpach (*loc. cit.*). These reactions called for further investigation, especially that which leads to the formation of *o*-4-xylidine from *m*-toluidine, in order that the yields obtainable by this and alternative methods might be compared.

Reactions have now been carried out at 210° to 280° between *m*-toluidine hydrochloride and various proportions of methyl alcohol. When the two reactants were used in equimolecular proportion at 210—235°, the main basic product was *o*-4-xylidine (I); there were no phenolic by-products, but a considerable quantity of methylated acridines was formed. With 2 mols. of methyl alcohol at 200—235° the main basic product was *ψ*-cumidine (II): again no phenolic by-products were encountered, but methylated acridines were formed. The best yield of *ψ*-cumidine, however, was obtained when 3 mols. of methyl alcohol were used at 210—220°. With 4 mols. of methyl alcohol at 260—280° the products were *iso*duridine (III), *iso*durenol, pentamethylphenol, and methylated acridines.

The aromatic bases formed in these reactions were purified by distillation with a Dufton column and identified by means of the melting point of the acetyl derivatives, together with a mixed melting point with an authentic specimen (aceto-*o*-xylidide has m. p. 99°, aceto-*ψ*-cumidide 165°, and aceto*iso*duridide 217°). Earlier work (Hey, *loc. cit.*) has shown that both phenols and acridine derivatives are formed as by-products during the Hofmann–Martius reaction. The tendency to phenol formation was shown to increase with the progressive introduction of methyl groups into the nucleus. This observation is supported in the present work, which also clearly demonstrates that the reactivity of the nuclear positions in these reactions is in the order $p > o > m$. It is also clear, in agreement with Liebermann and Kardos (*loc. cit.*), that the tendency for the formation of acridine derivatives is appreciably greater with *m*-toluidine than with *o*- and *p*-toluidine. In view of the earlier work by Liebermann and Kardos the acridine by-products were not examined in the present investigation.

The maximum yield of *o*-4-xylidine so far obtained by this method was of the order of 30%, calculated on *m*-toluidine hydrochloride in the one-stage process. The method used by Karrer, Becker, Benz, Frei, Salomon, and Schöpp (*Helv. Chim. Acta*, 1935, **18**, 1435) in the synthesis of riboflavin involves the nitration of pure *o*-xylene, the separation of 4- and 5-nitro-*o*-xylene, and the subsequent reduction of 4-nitro-*o*-xylene, the overall yield of *o*-4-xylidine being approximately 15%, calculated on *o*-xylene. The unsatisfactory character of Karrer's method has also been the subject of comment by Wisansky and Ansbacher (*J. Amer. Chem. Soc.*, 1941, **63**, 2532).

In earlier work on the Hofmann–Martius reaction (Hey, *loc. cit.*; see also Hey and Jackson, J., 1934, 645) it was conclusively proved that after methylation had been effected at the *p*- and *o*-positions with reference to the amino-group further methylation could take place at the *m*-positions, resulting finally in a fully methylated aromatic nucleus. Up to that time the possibility of *m*-alkylation was frequently denied and the persistence of this view may be traced back to the erroneous statements of Limpach (*loc. cit.*). It is unfortunate that in recent publications the same incorrect statements continue to be made. For example, in a reference to the Hofmann–Martius reaction in "The Organic Chemistry of Nitrogen" by N. V. Sidgwick (Ed. by T. W. J. Taylor and W. Baker, Oxford, 1937, p. 77), one finds "the *p*-alkyl-aniline is formed if the *p*-position is free and, if not, an *o*-alkyl-aniline can be formed, but the *m*-position is never occupied." The same misunderstanding is implicit in a statement due to Drumm, O'Connor, and Reilly (*J. Amer. Chem. Soc.*, 1940, **62**, 1241; see also

Watson, *Ann. Reports*, 1941, 123), who, in an examination of the products formed in the rearrangement of dibenzylaniline hydrochloride, reported the formation of *p*-aminodiphenylmethane, 1-amino-2 : 4-dibenzylbenzene, and a compound regarded as 1-amino-2 : 4 : 6-tribenzylbenzene and referred to the last as the first example of the introduction of more than two groups in this reaction. The present authors emphasise once again the fact that *m*-methylation in the Hofmann–Martius reaction has been established beyond question.

Experimental.

General Method.—The dry methyl alcohol and dry *m*-toluidine hydrochloride were heated in an iron autoclave of approximately 300 c.c. capacity immersed in an oil-bath. The autoclave was fitted with a pressure gauge and thermometer pocket but was without a stirrer. The product was distilled with steam, first from acid solution in order to remove phenols, and then from alkaline solution to remove volatile aromatic bases. The non-volatile residue, contaminated with some ferric hydroxide from the walls of the autoclave, was extracted repeatedly with hot benzene, which removed the acridine derivatives. The volatile aromatic bases were redistilled through a Dufton column. The following results were obtained :

(a) *With* 1 *mol. of methyl alcohol.* (i) A mixture of *m*-toluidine hydrochloride (48 g.) and methyl alcohol (11 g.) was heated at 215—220° for 6 hours. Steam-distillation from acid solution gave no phenols, but after basification volatile aromatic bases (10·5 g.; yield, 26%, calculated as xylidine on *m*-toluidine) were collected, which distilled at 210—230°. Redistillation gave mainly *o*-4-xylidine, b. p. 222—228°, m. p. 47—48° (acetyl derivative, m. p. and mixed m. p. 96—98°). The authentic specimen of aceto-*o*-4-xylidide was prepared by reduction of 4-nitro-*o*-xylene and subsequent acetylation. Evaporation of the benzene extract gave a mixture of methylated acridines (8·1 g.).

(ii) Repetition of this experiment at 210—235° for 8 hours gave no phenolic products, but volatile aromatic bases (14 g.; yield, 35%), b. p. 210—230°, which consisted mainly of *o*-4-xylidine, and methylated acridines (7 g.).

(b) *With* 2 *mols. of methyl alcohol.* *m*-Toluidine hydrochloride (48 g.) and methyl alcohol (22 g.) were heated together for 9 hours at 200—235°. No phenols were obtained, but steam-distillation from alkaline solution gave aromatic bases (17 g.), b. p. 225—240°. Redistillation gave mainly ψ-cumidine, b. p. 230—236°, m. p. 64° (acetyl derivative, m. p. and mixed m. p. 162—164°). The methylated acridines were not isolated.

(c) *With* 3 *mols. of methyl alcohol.* *m*-Toluidine hydrochloride (48 g.) and methyl alcohol (33 g.) were heated at 210—220° for 5½ hours. No phenolic products were obtained, but the volatile aromatic bases (24·5 g.; yield, 54%, calculated as ψ-cumidine on *m*-toluidine), b. p. 220—240°, consisted almost exclusively of ψ-cumidine, b. p. 232—236°, m. p. 64° (acetyl derivative, m. p. 163—164°). The benzene extract yielded a residue of methylated acridines (6·3 g.).

(d) *With* 4 *mols. of methyl alcohol.* (i) *m*-Toluidine hydrochloride (48 g.) and methyl alcohol (44 g.) were heated at 260—280° for 10 hours. Steam-distillation from acid solution gave a phenolic product (10·5 g.), which after repeated crystallisation from light petroleum yielded pentamethylphenol, m. p. and mixed m. p. 124—125°. Concentration of the mother-liquors deposited crude *iso*durenol, which after several crystallisations melted at 79—81°, both alone and on admixture with an authentic specimen. After basification volatile aromatic bases (16 g.) were collected which distilled at 255—260°. The bases solidified on cooling. Redistillation gave pure *iso*duridine, b. p. 258—259°, which on acetylation gave aceto*iso*duridide (white needles from alcohol), m. p. and mixed m. p. 217·5° (Found : C, 75·2; H, 8·8; N, 7·5. Calc. for $C_{12}H_{17}ON$: C, 75·4; H, 8·9; N, 7·3%). Evaporation of the benzene gave a residue of methylated acridines.

Imperial College of Science and Technology, London, S.W.7. [*Received, October* 12*th*, 1942.]

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7. β-3 : 4-*Methylenedioxyphenyliso*propylamine.

By J. Elks and D. H. Hey.

A method is described for the preparation of β-3 : 4-methylenedioxyphenyl*iso*propylamine from piperonal, which may be regarded as a prototype for a general method for the preparation of substituted β-phenyl*iso*propylamines from aromatic aldehydes.

Sympathomimetic amines related to amphetamine are conveniently prepared from the appropriate ketone, usually by the reduction of the oxime. Amphetamine itself is obtained in this way by the reduction of benzyl methyl ketoxime (Hey, J., 1930, 18). The preparation of similar bases with substituent groups in the aromatic nucleus is dependent on the accessibility of the corresponding substituted benzyl methyl ketones. Such ketones may be conveniently prepared by the method of Darzens (*Compt. rend.*, 1906, **142**, 214), which consists in the condensation of an aromatic aldehyde with an α-halogeno-aliphatic ester in presence of sodium ethoxide, followed by hydrolysis and decarboxylation of the resulting glycide ester, thus :

$$R{\cdot}CHO + R'{\cdot}CHCl{\cdot}CO_2Et \longrightarrow RCH\!\!\diagup\!\!\diagdown\!\!CR'{\cdot}CO_2Et \longrightarrow RCH\!\!\diagup\!\!\diagdown\!\!CR'{\cdot}CO_2H \longrightarrow R{\cdot}CH_2{\cdot}CO{\cdot}R'$$

(O)

In view of the recent publication of B.P. 519,894 (Robinson, Lowe, and Imperial Chemical Industries, Ltd.), which directs attention to this route to substituted β-phenyl*iso*propylamines from the corresponding substituted benzaldehydes, it is desired to place on record work on these lines commenced in 1939 but interrupted owing to the war. This work was undertaken with the object of developing this series of reactions as a general method for the preparation of substituted β-phenyl*iso*propylamines, many of which are already known to possess physiological activity of interest. The only synthesis completed was that of β-3 : 4-methylenedioxyphenyl*iso*propylamine and details of this preparation given below may serve as a prototype for the general method.

The condensation of piperonal with ethyl α-bromopropionate gave β-3 : 4-methylenedioxyphenyl-α-methylglycidic ester, which on subsequent hydrolysis and decarboxylation gave 3 : 4-methylenedioxybenzyl methyl ketone. Finally β-3 : 4-methylenedioxyphenyl*iso*propylamine was prepared from the latter by means of the Leuckart reaction, *i.e.*, heating the ketone with formamide and hydrolysing the resulting formyl derivative (cf. Ingersoll, Brown, Kim, Beauchamp, and Jennings, *J. Amer. Chem. Soc.*, 1936, **58**, 1808).

β-3 : 4-Methylenedioxyphenyl*iso*propylamine has been prepared by Mannich and Jacobsohn (*Ber.*, 1910, **43**, 194) by the reduction of the oxime of 3 : 4-methylenedioxybenzyl methyl ketone, which in turn was prepared by the action of heat on *iso*safrole oxide (Hoering, *Ber.*, 1905, **38**, 3481). Several workers have prepared 3 : 4-methylenedioxybenzyl methyl ketone from derivatives of *iso*safrole.

Experimental.

3 : 4-*Methylenedioxybenzyl Methyl Ketone.*—Freshly prepared powdered sodium ethoxide (23 g.) was added during 4 hours to a stirred mixture of piperonal (50 g.) and ethyl α-bromopropionate (61 g.) cooled in ice–salt. Stirring was continued overnight at room temperature and for 6 hours on the water-bath; ice-water was then added, and the mixture acidified with dilute acetic acid. The glycide ester was extracted with ether, and the ethereal solution washed with aqueous sodium carbonate and dried with sodium sulphate. After removal of ether the residue was distilled and collected between 70° and 200° at 20 mm. Subsequent redistillation gave β-3 : 4-methylenedioxyphenyl-α-methylglycide ester (40 g.), b. p. 184—186°/14 mm. (yield, 48%). Darzens (*loc. cit.*) recorded b. p. 205—210°/25 mm. The ester (35 g.) was refluxed for 5 hours with a solution of sodium hydroxide (10 g.) in 90% aqueous alcohol (150 c.c.). After removal of part of the alcohol by distillation the residue was diluted with a large volume of water and extracted with a small quantity of ether. The aqueous layer was acidified with dilute hydrochloric acid, the mixture extracted with ether, and the extract dried over sodium sulphate. The free acid obtained on removal of the ether was refluxed for 18 hours at 180° with the addition of a trace of copper powder; the liquid was then distilled slowly under reduced pressure in the presence of copper powder. Redistillation of the product gave 3 : 4-methylenedioxybenzyl methyl ketone (11·1 g.), b. p. 154—156°/11 mm. (yield, 44·5%). Mannich and Jacobsohn (*loc. cit.*) recorded b. p. 168°/17 mm. and Hoering (*loc. cit.*) b. p. 149—151°/10 mm. The semicarbazone, prepared in the usual manner, separated from aqueous alcohol in white needles, m. p. 161—162°. Wallach and Müller (*Annalen*, 1904, **332**, 333) recorded m. p. 163°.

β-3 : 4-*Methylenedioxyphenylisopropylamine.*—Ammonium formate (14 g.) was heated under distillation conditions to 160°, the water which was collected being rejected : the ketone (9·9 g.) was then added and the temperature maintained at 160—165°. The ketone which distilled over was returned to the reaction flask from time to time. The heating was continued for 5 hours after the distillation of water ceased. The mixture was allowed to cool and was shaken with twice its volume of water. The formyl derivative of the amine was extracted with ether, the ether removed, and the residual oil hydrolysed by refluxing with hydrochloric acid (*d* 1·16; 8 c.c.) for 45 minutes. To the cooled mixture, more hydrochloric acid (2 c.c.) was added, and the whole extracted with ether. The aqueous layer was then made alkaline and again extracted with ether, the extract dried over potash, the ether removed, and the residue distilled under reduced pressure. β-3 : 4-Methylenedioxyphenyl*iso*propylamine (2·0 g.) was collected at 138—140°/12 mm. (yield, 20%) (Found : C, 66·8; H, 7·2. Calc. for $C_{10}H_{13}O_2N$: C, 67·0; H, 7·3%). Mannich and Jacobsohn (*loc. cit.*) recorded b. p. 157°/22 mm. A portion of the amine (1 g.) was warmed with acetic anhydride (1 g.) on the steam-bath for 30 minutes. The liquid was poured into water, and the mixture boiled for a few minutes and cooled. The solid obtained melted at 59—61° after crystallisation from aqueous alcohol and drying in air. After a second crystallisation from aqueous alcohol, followed by drying in a vacuum, the m. p. was raised to 93°. Direct crystallisation from benzene–light petroleum also gave the *acetyl* derivative in white fibrous needles, m. p. 93° (Found : N, 6·35. $C_{12}H_{15}O_3N$ requires N, 6·3%). The acetyl derivative of amphetamine (Hey, *loc. cit.*) exhibits a similar behaviour.

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8. *Physical Properties and Chemical Constitution. Part VII. Alkyl Sulphides, Disulphides, Sulphites, Sulphates, and Orthophosphates.*

By Arthur I. Vogel and David M. Cowan.

The refractive indices for the C, D, F, and G′ lines at 20·0°, and the surface tensions and densities over a range of temperatures, have been determined for numerous alkyl compounds, particularly sulphides and disulphides. The molecular refractivities and parachors have been evaluated. The data obtained have been employed in the calculation of preliminary values for the constants of sulphur and for the contribution of the oxygen atom in alkyl sulphites and sulphates.

The literature contains but few trustworthy experimental results from which the physical constants (refractivities, molecular refraction coefficient, and parachor) of sulphur may be deduced (compare Eisenlohr, "Spektrochemie organischer Verbindungen," 1912, pp. 64 *et seq.*; Sugden, Reed, and Wilkins, J., 1925, **127**, 1533; Baroni, *Atti R. Accad. Lincei*, 1931, **14**, 28; Bezzi, *Gazzetta*, 1935, **65**, 693). The most satisfactory method for evaluating the constants for sulphur is from dialkyl sulphides : new data for a comprehensive series of such compounds are now presented. Since trustworthy figures for carbon and hydrogen are not available (largely because of the uncertainty of the CH_2 value), the necessary calculations will be made in a future communication. For the present, attention is directed to the following results for the various isomeric sulphides.*

Isomeric Alkyl Sulphides.

	P.	R_C.	R_D.	R_F.	$R_{G'}$.	$Mn_D^{20°}$.
$MeBu^{\alpha}S$	280·1	32·92	33·10	33·53	33·94	150·93
$MeBu^{\beta}S$	279·6	32·99	33·17	33·60	33·93	150·41
$MeBu^{\gamma}S$	277·9	33·10	33·29	33·73	34·08	150·14
$EtBu^{\alpha}S$	320·3	37·68	37·89	38·38	38·75	171·29
$EtBu^{\gamma}S$	317·2	37·93	38·12	38·63	39·02	170·44
Bu^{α}_2S	399·3	46·82	47·06	47·64	48·10	212·54
Bu^{β}_2S	395·4	47·04	47·29	47·90	48·32	211·65
sec.-Bu_2S	395·0	46·90	47·14	47·74	48·19	212·19

* For significance of abbreviations in the Table, see p. 18.

The facile conversion of thiols into disulphides by means of iodine, $2RS^- + I_2 = R{\cdot}S{\cdot}S{\cdot}R$ (I.) + $2I^-$, would seem to support formula (I) for disulphides (compare *X*-ray studies of Egartner, Halla, and Schacherl, *Z. physikal. Chem.*, 1932, *B*, **18**, 189). By subtracting the experimental values for sulphides from those of disulphides, a direct determination of the sulphur contribution is obtained. The results are collected below. This, of course, will correspond to linkages of the type C·S·S and may not be identical with C·S·C (deducible from alkyl sulphides alone) (compare Smyth, " Dielectric Constant and Molecular Structure," 1931, p. 152).

Values for Sulphur ($R_2S_2 - R_2S$).

R.	*P.*	R_C.	R_D.	R_F.	$R_{G'}$.	$Mn_D^{20°}$.
Methyl	50·8	7·95	8·02	8·21	8·39	54·53
Ethyl	49·6	8·05	8·14	8·30	8·45	54·13
n-Propyl	49·6	8·04	8·11	8·30	8·47	53·85
*iso*Propyl	50·1	8·02	8·06	8·28	8·42	53·98
n-Butyl	48·4	8·10	8·15	8·35	8·49	53·65
*iso*Butyl	48·0	7·90	7·98	8·14	8·33	53·49
n-Amyl	47·6	8·12	8·21	8·41	8·57	53·44
*iso*Amyl	48·3	7·97	8·04	8·23	8·41	53·53
Mean	49·1	8·019	8·089	8·278	8·441	53·78

The results for isomeric disulphides are presented in the next table.

Isomeric Alkyl Disulphides.

	P.	R_C.	R_D.	R_F.	$R_{G'}$.	$Mn_D^{20°}$.
$Bu^{\alpha}{}_2S_2$	447·7	54·92	55·21	55·99	56·59	266·19
$Bu^{\beta}{}_2S_2$	443·4	54·94	55·27	56·04	56·65	265·14
$Bu^{\gamma}{}_2S_2$	440·9	55·54	55·87	56·68	57·31	265·73

In order to provide information as to the nature of the linkage in sulphites and sulphates, measurements have been made on alkyl sulphites and sulphates. By comparison with the corresponding sulphides ($R_2SO_3 - R_2S$ and $R_2SO_4 - R_2S$), the contribution of the oxygen atom may be calculated. The final results are in the following tables.

Contribution of the Oxygen Atom in Alkyl Sulphites, ($R_2SO_3 - R_2S$)/3.

R.	*P.*	R_C.	R_D.	R_F.	$R_{G'}$.	$Mn_D^{20°}$.
Methyl	18·9	1·113	1·110	1·103	1·097	22·00
Ethyl	18·7	1·123	1·127	1·107	1·097	21·79
n-Propyl	18·8	1·167	1·167	1·157	1·147	21·82
*iso*Propyl	18·9	1·090	1·077	1·073	1·057	21·66
n-Butyl	18·1	1·147	1·150	1·140	1·123	20·98
*iso*Butyl	18·4	1·093	1·090	1·073	1·073	21·86
n-Amyl	18·3	1·143	1·140	1·140	1·120	21·82
*iso*Amyl	17·9	1·087	1·080	1·070	1·060	21·96
Mean	18·5	1·120	1·118	1·108	1·097	21·74

Contribution of the Oxygen Atom in Alkyl Sulphates, ($R_2SO_4 - R_2S$)/4.

Methyl	18·7	0·818	0·813	0·790	0·775	21·45
Ethyl	18·7	0·815	0·810	0·780	0·758	21·46
n-Propyl	18·3	0·800	0·793	0·768	0·745	21·57
n-Butyl	17·9	0·808	0·800	0·775	0·753	21·58
Mean	18·2	0·810	0·804	0·778	0·758	21·52

The low values for the refractivities as well as their *decrease* in the series $R_C \longrightarrow R_{G'}$ are noteworthy [compare, *e.g.*, R_D for O (carbonyl) 2·211, O (ether) 1·643, O (hydroxyl) 1·525; Eisenlohr, *op. cit.*, 1912, p. 48; *Z. physikal. Chem.*, 1911, **75**, 585] : these provide new evidence for co-ordinate links in sulphites and sulphates. The subject will be discussed in detail, particularly from the viewpoint of the refraction of election groups (von Steiger, *Ber.*, 1921, **54**, 1381; Smyth, *Phil. Mag.*, 1925, **50**, 361; *op. cit.*, p. 150; Fajans and Knorr, *Ber.*, 1926, **59**, 249), in a later communication.

Measurements upon trialkyl orthophosphates have also been made, but detailed parallel calculations cannot be given because suitable data on the constants of phosphorus are lacking. However, from the scanty refractivity data available [R_D for PEt_3 at 18·6° (Zecchini, *Gazzetta*, 1893, **23**, 97; 1894, **24**, 34); R_C, R_D, and R_F for $PPr^{\alpha}{}_3$ and $PBu^{\alpha}{}_3$ at 25° (Jones, Davies, and Dyke, *J. Physical Chem.*, 1933, **37**, 584)] analogous results are obtained (see below).

Contribution of the Oxygen Atom in Trialkyl Phosphates ($R_3PO_4 - R_3P$)/4.

R.	R_C.	R_D.	R_F.
Ethyl	—	0·370	—
n-Propyl	0·450	0·430	0·375
n-Butyl	0·493	0·435	0·433

A comparison of the properties of *s.*- and *as.*-ethyl sulphite (ethyl ethanesulphonate) is given below.

	P.	R_C.	R_D.	R_F.	$R_{G'}$.	$Mn_D^{20°}$.
s.-Ethyl sulphite	297·6	31·76	31·91	32·27	32·54	196·44
as.- " "	293·4	30·15	30·21	30·57	30·77	196·27

Experimental.

Physical Measurements.—The surface tensions and refractive indices were determined exactly as described in earlier papers (*e.g.*, Part III, J., 1938, 1325). Four Pyrex surface-tension apparatus *A*, *B*, *C*, and *D* were used, the constants of which, determined with " AnalaR " sodium-dried benzene, were 1·8725, 2·3449, 2·3740, and 2·4696 respectively. Except where another apparatus is specified, apparatus *A* was used. In the determination of the densities, the sample and *all* the apparatus (pycnometer, and the small container for filling it with the sample) were kept in the thermostat at 20° ± 0·01° for at least 3 hours before the actual measurements; the room temperature was maintained as near 20° as possible. This procedure probably gave more trustworthy values of $d_{4^\circ}^{20\cdot0^\circ}$ than those obtained in the earlier measurements.

For convenience of reference all the compounds studied in this and future communications will be numbered in Clarendon type. In the tabulated results t is the temperature, h is the observed difference in height (in mm.) in the two arms of the U-tube, H the corrected value, $d_{4^\circ}^{t^\circ}$ the density (calculated from the observed densities by assuming a linear variation with temperature), γ the surface tension (dynes/cm.) computed from the equation $\gamma = KHd$, P the parachor, and $Mn_D^{20^\circ}$ the molecular refraction coefficient. The parachor was calculated in the usual way, allowance for the density of the vapour (computed by Sugden's method, J., 1925, **127**, 1540) being made when the temperature of measurement was within 60° of the b. p. All the measurements of the refractive indices were carried out at 20° ± 0·02°. Where 20° is used, 20·0° is to be understood; n_C, n_D, n_F, $n_{G'}$ are to be taken as referring to $n_C^{20\cdot0^\circ}$, etc.; and R_C, etc., to $[R_L]_C$, etc. Unless otherwise stated, all b. p.'s are corrected.

Previous Work.—Parachor values, the source of which is not indicated, are taken from Sidgwick, Sugden, and Adam (*Brit. Assoc. Rep.*, 1932, 265). Reference is also made to what appears to be the most trustworthy of the earlier values of the refractive indices for comparison; an exhaustive survey of all previous work would serve no useful purpose.

Disulphides and Sulphides.—Most of the original measurements were made with samples supplied by Eastman Kodak. These were rigorously purified by chemical methods and by distillation until $d_{4^\circ}^{20^\circ}$ and $n_D^{20^\circ}$ were constant. Some of the samples were prepared by us (sulphides from alkyl bromides and anhydrous sodium sulphide in alcoholic solution, and disulphides by oxidation of a solution of the sodium thiol with iodine); excellent agreement was obtained in the physical properties of the synthetic and the purchased samples. In order to economise space the results of the measurements on the duplicate preparations will not be given.

The disulphides were first distilled, and the middle fraction was mechanically shaken with one-third of its volume of 5—10% sodium hydroxide solution, this treatment with alkali being repeated twice; the products were then washed with distilled water until neutral, dried with calcium chloride (shaking machine for ½ hour), kept overnight over fresh calcium chloride, filtered, and again dried by shaking with the same desiccant, and distilled to constant $d_{4^\circ}^{20^\circ}$ and $n_D^{20^\circ}$.

The sulphides were similarly purified except that 10—15% alkali solution was used and that for those thio-ethers which were distilled at atmospheric pressure, the final distillation was made from sodium. Where distillation under diminished pressure was necessary, the purified sulphide was first dried over calcium chloride, then refluxed over sodium at 120° for at least 6 hours, filtered, and distilled under diminished pressure to constant $d_{4^\circ}^{20^\circ}$ and $n_D^{20^\circ}$.

1. *Dimethyl disulphide* (Eastman Kodak). B. p. 109·5°/774 mm.; M 94·19; n_C 1·52167, n_D 1·52599, n_F 1·53690, $n_{G'}$ 1·54573; R_C 26·97, R_D 27·15, R_F 27·62, $R_{G'}$ 28·00; $R_{G'-C}$ 1·03, R_{F-C} 0·65; $Mn_D^{20^\circ}$ 143·73. Densities determined: $d_{4^\circ}^{20^\circ}$ 1·0647, $d_{4^\circ}^{41\cdot5^\circ}$ 1·0391, $d_{4^\circ}^{61\cdot9^\circ}$ 1·0162, $d_{4^\circ}^{88\cdot5^\circ}$ 0·9886.

t.	h.	H.	$d_{4^\circ}^{t^\circ}$.	γ.	P.	t.	h.	H.	$d_{4^\circ}^{t^\circ}$.	γ.	P.
14·1°	13·95	13·71	1·0715	34·87	213·6	62·3°	12·02	11·78	1·0157	28·40	214·1
41·0	12·89	12·65	1·0397	31·22	214·1					Mean	213·9

2. *Diethyl disulphide.* This was prepared by a modification of Kekulé and Linnemann's method (*Annalen*, 1862, **123**, 277). 77 G. of ethylthiol (Eastman Kodak, b. p. 35°/768 mm.) were dissolved in 350 c.c. of 15% sodium hydroxide solution (calculated quantity for the formation of SEtNa) contained in a 1-litre three-necked Pyrex flask fitted with a mechanical stirrer and a double-surface condenser. Stirring was continued until all the thiol had reacted; the flask was cooled in ice. With constant stirring, 135 g. of pure iodine were gradually added (2 hours) by momentarily removing the rubber bung from the third aperture of the flask and replacing it immediately the iodine had been added. After each addition, the iodine gradually disappeared and an oily layer formed on the surface of the liquid. The mixture was stirred for a further 2·5 hours and kept for 2·5 hours. The colourless upper layer was separated, and the aqueous layer extracted with ether; the combined liquids were washed with one-third the volume of 15% sodium hydroxide solution, then twice with water, and partly dried with calcium chloride, and the ether removed. The resultant colourless liquid was shaken three times with one-third of its volume of 5% sodium hydroxide solution, washed with water until free from alkali, and dried with calcium chloride. The yield of crude product was 53·5 g. (70%); the main bulk boiled constantly at 152°/754 mm.; a middle fraction was collected for the physical measurements. B. p. 152°/754 mm.; M 122·24; n_C 1·50329, n_D 1·50704, n_F 1·51653, $n_{G'}$ 1·52404; R_C 36·44, R_D 36·67, R_F 37·25, $R_{G'}$ 37·70; $R_{G'-C}$ 1·26, R_{F-C} 0·81; $Mn_D^{20^\circ}$ 184·21. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·9920, $d_{4^\circ}^{43\cdot6^\circ}$ 0·9702, $d_{4^\circ}^{60\cdot7^\circ}$ 0·9534, $d_{4^\circ}^{90\cdot5^\circ}$ 0·9246.

17·3°	16·99	16·75	0·9946	31·19	290·5	61·4°	15·10	14·86	0·9527	26·51	291·1
41·1	16·05	15·81	0·9726	28·79	291·1	86·2	14·07	13·83	0·9288	24·05	291·5
										Mean	291·1

(Baroni, *loc. cit.*, gives $d_{4^\circ}^{20^\circ}$ 0·9926, P 287·6; Bezzi, *loc. cit.*, gives b. p. 152—154°/760 mm., $d_{4^\circ}^{20^\circ}$ 0·9927, $n_D^{20^\circ}$ 1·5070.)

3. *Di-n-propyl disulphide* (Eastman Kodak). B. p. 193·5°/750 mm.; M 150·29; n_C 1·49465, n_D 1·49813, n_F 1·50679, $n_{G'}$ 1·51359; R_C 45·63, R_D 45·90, R_F 46·58, $R_{G'}$ 47·11; $R_{G'-C}$ 1·48, R_{F-C} 0·95; $Mn_D^{20^\circ}$ 225·15. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·9599, $d_{4^\circ}^{61\cdot2^\circ}$ 0·9237, $d_{4^\circ}^{86\cdot7^\circ}$ 0·9010.

18·8°	17·29	17·05	0·9609	30·68	368·1	87·3°	14·40	14·16	0·9004	23·87	369·0
61·8	15·43	15·19	0·9232	26·26	368·5					Mean	368·5

(Bezzi, *loc. cit.*, gives b. p. 191—192°/760 mm., $d_{4^\circ}^{20^\circ}$ 0·9525, $n_D^{20^\circ}$ 1·4981.)

4. *Diisopropyl disulphide.* This was prepared as for diethyl disulphide except that the iodine was dissolved in 40% aqueous potassium iodide solution, thus permitting the use of a dropping funnel. The quantities used were: 24 g. of *iso*propylthiol (Eastman Kodak, b. p. 50—51°/753 mm.), 12·6 g. of sodium hydroxide dissolved in 85 c.c. of water in a 500-c.c. three-necked flask, and 38 g. (slight defect below theoretical quantity) of iodine in 100 c.c. of 40% aqueous potassium iodide solution. The yield of the crude product was 14 g. B. p. 176°/767 mm.; M 150·29; n_C 1·48812, n_L 1·49164, n_F 1·50021, $n_{G'}$ 1·50687; R_C 45·90, R_D 46·18, R_F 46·87, $R_{G'}$ 47·40; $R_{G'-C}$ 1·50, R_{F-C} 0·86; $Mn_D^{20^\circ}$ 224·17. Densities determined: $d_{4^\circ}^{20^\circ}$ 0·9435, $d_{4^\circ}^{41\cdot7^\circ}$ 0·9247, $d_{4^\circ}^{59\cdot6^\circ}$ 0·9085, $d_{4^\circ}^{87\cdot4^\circ}$ 0·8853.

Apparatus *B*.

t.	*h.*	*H.*	$d^{t°}_{4°}$	γ.	*P.*	*t.*	*h.*	*H.*	$d^{t°}_{4°}$	γ.	*P.*
18·4°	13·15	12·91	0·9449	28·60	367·8	63·0°	11·59	11·35	0·9055	24·06	367·6
41·9	12·37	12·13	0·9245	26·30	368·1	86·4	10·94	10·70	0·8862	22·24	368·3
										Mean	368·0

5. *Di*-n-*butyl disulphide* (Eastman Kodak). B. p. 230·5°/755 mm., 84°/3 mm.; *M* 178·34; n_C 1·48950, n_D 1·49259, n_F 1·50079, $n_{G'}$ 1·50712; R_C 54·92, R_D 55·21; R_F 55·99, $R_{G'}$ 56·59; $R_{G'-C}$ 1·67, R_{F-C} 1·07; $Mn_D^{20°}$ 266·19. Densities determined: $d^{20°}_{4°}$ 0·9383, $d^{60·4°}_{4°}$ 0·9044, $d^{85·9°}_{4°}$ 0·8840.

15·5°	17·82	17·58	0·9419	31·01	446·8	86·3°	15·00	14·76	0·8837	24·42	448·3
61·4	15·96	15·72	0·9036	26·60	448·0					Mean	447·7

(Bezzi, *loc. cit.*, gives b. p. 143—144°/83 mm., $d^{20°}_{4°}$ 0·9306, $n_D^{20°}$ 1·49208.)

6. *Diisobutyl disulphide*. This was prepared and purified as described under **2**. 43·5 G. of *iso*butylthiol (Eastman Kodak, b. p. 87·5°/764 mm.), 135 c.c. of 15% sodium hydroxide solution, and 52 g. of solid iodine yielded 37 g. of crude disulphide. B. p. 215°/767 mm. and 76·5°/5 mm.; *M* 178·34; n_C 1·48342, n_D 1·48666, n_F 1·49471, $n_{G'}$ 1·50102; R_C 54·94, R_D 55·27, R_F 56·04, $R_{G'}$ 56·65; $R_{G'-C}$ 1·71, R_{F-C} 1·10; $Mn_D^{20°}$ 265·14. Densities determined: $d^{20°}_{4°}$ 0·9275, $d^{41·4°}_{4°}$ 0·9090, $d^{61·6°}_{4°}$ 0·8922, $d^{86·3°}_{4°}$ 0·8718.

17·1°	16·49	16·25	0·9298	28·29	442·2	60·7°	14·80	14·56	0·8929	24·34	443·7
41·6	15·53	15·29	0·9088	26·02	443·2	86·2	13·87	13·63	0·8719	22·25	444·3
										Mean	443·4

7. *Di*-tert.-*butyl disulphide*. This was prepared from 30 g. of *tert.*-butylthiol (Eastman Kodak, b. p. 63—64°/753 mm., $d^{20°}_{4°}$ 0·7985, $n_D^{20°}$ 1·42246), 94 c.c. of 15% sodium hydroxide solution, and 36 g. of iodine dissolved in 100 c.c. of 40% aqueous potassium iodide solution. The yield of pure product was 18 g. B. p. 64°/5·5 mm. (Rheinboldt, Mott, and Motzkus, *J. pr. Chem.*, 1932, **134**, 257, give b. p. 72°/11 mm.); *M* 178·34; n_C 1·48664, n_D 1·49003, n_F 1·49844, $n_{G'}$ 1·50501; R_C 55·54, R_D 55·87, R_F 56·68, $R_{G'}$ 57·31; $R_{G'-C}$ 1·77, R_{F-C} 1·12; $Mn_D^{20°}$ 265·73. Densities determined: $d^{20°}_{4°}$ 0·9229, $d^{43·7°}_{4°}$ 0·9039, $d^{60·4°}_{4°}$ 0·8906, $d^{84·3°}_{4°}$ 0·8713.

17·5°	16·02	15·78	0·9249	27·33	440·9	64·8°	14·14	13·90	0·8871	23·09	440·7
41·5	15·09	14·85	0·9057	25·18	441·1	87·9	13·29	13·05	0·8684	21·22	440·8
										Mean	440·9

8. *Di*-n-*amyl disulphide* (Eastman Kodak). B. p. 119°/7 mm.; *M* 206·40; n_C 1·48549, n_D 1·48887, n_F 1·49673, $n_{G'}$ 1·50280; R_C 64·21, R_D 64·59, R_F 65·47, $R_{G'}$ 66·15; $R_{G'-C}$ 1·94, R_{F-C} 1·26; $Mn_D^{20°}n$ 307·31. Densities determined: $d^{20°}_{4°}$ 0·9221, $d^{61·7°}_{4°}$ 0·8906, $d^{87·1°}_{4°}$ 0·8708, $d^{120·7°}_{4°}$ 0·8444.

18·5°	17·43	17·19	0·9233	29·72	522·0	87·1°	15·16	14·92	0·8708	24·33	526·4
61·0	15·96	15·72	0·8911	26·23	524·3	120·7	13·76	13·52	0·8444	21·38	525·6
										Mean	524·6

9. *Diisoamyl disulphide* (Eastman Kodak). B. p. 115°/9 mm.; *M* 206·40; n_C 1·48320, n_D 1·48637, n_F 1·49423, $n_{G'}$ 1·50035; R_C 64·15, R_D 64·51, R_F 65·39, $R_{G'}$ 66·09; $R_{G'-C}$ 1·94, R_{F-C} 1·24; $Mn_D^{20°}$ 306·79. Densities determined: $d^{20°}_{4°}$ 0·9192, $d^{61·5°}_{4°}$ 0·8854, $d^{86·6°}_{4°}$ 0·8655, $d^{121·5°}_{4°}$ 0·8378.

Apparatus *C*.

13·4°	13·49	13·25	0·9245	29·08	518·5	86·8°	11·41	11·17	0·8653	22·95	522·1
61·7	12·11	11·87	0·8852	24·94	521·1	120·2	10·48	10·24	0·8388	20·39	522·9
										Mean	521·2

10. *Methyl sulphide* (Eastman Kodak). B. p. 37·8°/765 mm.; *M* 62·13; n_C 1·43272, n_D 1·43570, n_F 1·44310, $n_{G'}$ 1·44831; R_C 19·02, R_D 19·13, R_F 19·41, $R_{G'}$ 19·61; $R_{G'-C}$ 0·59, R_{F-C} 0·39; $Mn_D^{20°}$ 89·20. Densities determined: $d^{20°}_{4°}$ 0·8486, $d^{25·0°}_{4°}$ 0·8456.

A	12·9°	15·87	15·63	0·8529	24·96	163·0	*C*	14·5°	12·60	12·36	0·8519	25·00	163·3
B	17·3	12·60	12·36	0·8502	24·64	163·0						Mean	163·1

11. *Methyl ethyl sulphide* (Eastman Kodak). B. p. 66°/747 mm.; *M* 76·15; n_C 1·43744, n_D 1·44033, n_F 1·44697, $n_{G'}$ 1·45306; R_C 23·62, R_D 23·75, R_F 24·06, $R_{G'}$ 24·35; $R_{G'-C}$ 0·73, R_{F-C} 0·44; $Mn_D^{21°}$ 109·68. Densities determined: $d^{6·5°}_{4°}$ 0·8557, $d^{20°}_{4°}$ 0·8455, $d^{40·7°}_{4°}$ 0·8203.

A	6·5°	16·84	16·60	0·8603	26·74	201·4	*B*	7·6°	13·41	13·17	0·8580	26·50	201·5
A	16·5	16·35	16·11	0·8494	25·62	201·8	*B*	22·3	12·85	12·61	0·8430	24·93	202·0
A	40·9	14·82	14·58	0·8201	22·39	202·3	*B*	41·3	11·79	11·55	0·8196	22·20	202·0
												Mean	201·9

12. *Ethyl sulphide*. This was prepared by distilling an aqueous solution of sodium ethyl sulphate with excess of sodium sulphide until the temperature of the reaction mixture was 120°. The sulphide layer in the aqueous distillate was removed, shaken several times with 20% sodium hydroxide solution, then kept over sodium hydroxide pellets for 24 hours, washed with water until neutral, dried with calcium chloride, and distilled over sodium. B. p. 92°/761 mm.; *M* 90·18; n_C 1·43987, n_D 1·44235, n_F 1·44979, $n_{G'}$ 1·45523; R_C 28·39, R_D 28·53, R_F 28·95, $R_{G'}$ 29·25; $R_{G'-C}$ 0·86, R_{F-C} 0·56; $Mn_D^{20°}$ 130·08. Densities determined: $d^{20°}_{4°}$ 0·8369, $d^{41·4°}_{4°}$ 0·8155, $d^{60·5°}_{4°}$ 0·7961.

13·5°	16·61	16·37	0·8434	25·85	241·1	61·5°	14·04	13·80	0·7950	20·54	241·9
41·3	15·14	14·90	0·8156	22·75	241·5					Mean	241·5

(Baroni, *loc. cit.*, gives $d^{20°}_{4°}$ 0·8367, $\gamma_{20°}$ 22·19, *P* 239·1; Bezzi, *loc. cit.*, gives b. p. 93—94°/760 mm., $d^{20°}_{4°}$ 0·8278, $n_D^{20°}$ 1·44303.)

13. n-*Propyl sulphide* (Eastman Kodak). B. p. 142°/762 mm.; *M* 118·23; n_C 1·44622, n_D 1·44896, n_F 1·45567 $n_{G'}$ 1·46077; R_C 37·59, R_D 37·79, R_F 38·28, $R_{G'}$ 38·64; $R_{G'-C}$ 1·05, R_{F-C} 0·69; $Mn_D^{20°}$ 171·30. Densities determined $d_4^{20°}$ 0·8391, $d_4^{61·5°}$ 0·8013, $d_4^{85·5°}$ 0·7804.

t.	*h.*	*H.*	$d_{4°}^{t°}$	*γ.*	*P.*	*t.*	*h.*	*H.*	$d_{4°}^{t°}$	*γ.*	*P.*
16·4°	17·19	16·95	0·8423	26·72	319·1	86·7°	13·60	13·36	0·7791	19·49	318·8
61·9	14·77	14·53	0·8013	21·80	318·8					Mean	318·9

(Mann and Purdie, J., 1935, 1549, give b. p. 139°, $d^{24°}$ 0·84315; Bezzi, *loc. cit.*, gives b. p. 140—143°/760 mm., $d_4^{20°}$ 0·8302, $n_D^{20°}$ 1·44904.)

14. iso*Propyl sulphide.* This was prepared by adding 181 g. of *iso*propyl bromide, b. p. 59—59·5°/765 mm., slowly to a boiling mixture of 224 g. of finely-powdered anhydrous sodium sulphide and excess of rectified spirit, the whole refluxed for 7 hours, and the alcohol distilled off (compare Winssinger, *Bull. Soc. chim.*, 1887, **48**, 109; Mann and Purdie, *loc. cit.*). The distillate was diluted with excess of water, and the crude sulphide (70 g.) purified in the usual manner with 10% sodium hydroxide solution, etc. B. p. 119°/761 mm.; *M* 118·23; n_C 1·43628, n_D 1·43950, n_F 1·44574, $n_{G'}$ 1·45093; R_C 37·88, R_D 38·12, R_F 38·59, $R_{G'}$ 38·98; $R_{G'-C}$ 1·10, R_{F-C} 0·71; $Mn_D^{20°}$ 170·19. Densities determined: $d^{20°}$ 0·8166, $d_4^{41·4°}$ 0·7960, $d_4^{61·2°}$ 0·7775, $d_4^{87·4°}$ 0·7534.

Apparatus *B*.

9·5°	12·78	12·54	0·8266	24·31	317·6	60·6°	10·76	10·52	0·7781	19·19	318·2
42·3	11·42	11·18	0·7951	20·84	317·7	86·2	9·75	9·51	0·7545	16·83	318·1
										Mean	317·9

(Mann and Purdie, *loc. cit.*, give b. p. 120°.)

15. n-*Butyl sulphide* (Eastman Kodak). B. p. 187°/765 mm.; *M* 146·28; n_C 1·45031, n_D 1·45297, n_F 1·45954, $n_{G'}$ 1·46458; R_C 46·82, R_D 47·06, R_F 47·64, $R_{G'}$ 48·10; $R_{G'-C}$ 1·28, R_{F-C} 0·82; $Mn_D^{20°}$ 212·54. Densities determined: $d_4^{20°}$ 0·8402, $d_4^{61·2°}$ 0·8040, $d_4^{86·1°}$ 0·7843.

Apparatus *B*.

18·3°	14·12	13·88	0·8417	27·40	397·6	87·8°	11·65	11·41	0·7828	20·94	400·0
61·7	12·66	12·42	0·8036	23·40	400·4					Mean	399·3

(Mann and Purdie, *loc. cit.*, give b. p. 185—185·5°, $d^{24°}$ 0·8352, $\gamma_{24°}$ 26·45, *P* 395·5; Bezzi, *loc. cit.*, gives b. p. 182—184°/760 mm., $d_4^{20°}$ 0·8334, n_D^{20} 1·45405.)

16. iso*Butyl sulphide* (Eastman Kodak). B. p. 169°/772 mm.; *M* 146·28; n_C 1·44420, n_D 1·44686, n_F 1·45353, $n_{G'}$ 1·45823; R_C 47·04, R_D 47·29, R_F 47·90, $R_{G'}$ 48·32; $R_{G'-C}$ 1·28, R_{F-C} 0·86; $Mn_D^{20°}$ 211·65. Densities determined: $d_4^{20°}$ 0·8263, $d_4^{41·5°}$ 0·8106, $d_4^{62·7°}$ 0·7918, $d_4^{87·5°}$ 0·7712.

14·7°	16·60	16·36	0·8306	25·44	395·5	62·3°	14·38	14·14	0·7922	20·98	395·2
41·1	15·39	15·15	0·8107	23·00	395·1	88·2	13·32	13·08	0·7706	18·87	395·7
										Mean	395·4

(Mann and Purdie, *loc. cit.*, give b. p. 174°, $d^{24°}$ 0·8301, $\gamma_{24°}$ 24·90, *P* 392·8.)

17. sec.-*Butyl sulphide.* This was prepared from 68·5 g. of *sec.*-butyl bromide, b. p. 90·5—92°/756 mm., 58·5 g. of finely-powdered anhydrous sodium sulphide, and 200 c.c. of boiling rectified spirit as detailed under **14**. The yield of crude thio-ether was 26 g. B. p. 164·5°/739 mm.; *M* 146·28; n_C 1·44793, n_D 1·45062, n_F 1·45715, $n_{G'}$ 1·46220; R_C 46·90, R_D 47·14, R_F 47·74, $R_{G'}$ 48·19; $R_{G'-C}$ 1·29, R_{F-C} 0·84; $Mn_D^{20°}$ 212·19. Densities determined: $d_4^{20°}$ 0·8348, $d_4^{41·3°}$ 0·8163, $d_4^{61·3°}$ 0·7996, $d_4^{85·0°}$ 0·7800.

Apparatus *C*.

12·0°	13·53	13·29	0·8416	26·55	394·6	62·0°	11·76	11·52	0·7990	21·85	395·7
25·2	13·12	12·88	0·8304	25·39	395·4	85·6	10·76	10·52	0·7795	19·47	394·2
40·8	12·46	12·22	0·8167	23·69	395·2					Mean	395·0

tert.-*Butyl sulphide.* All attempts to prepare this compound from *tert.*-butyl bromide, b. p. 72·5—73·5°/765 mm., and anhydrous sodium sulphide in alcoholic solution were unsuccessful.

18. n-*Amyl sulphide* (Eastman Kodak). B. p. 84·5°/4 mm.; *M* 174·34; n_C 1·45352, n_D 1·45617, n_F 1·46262, $n_{G'}$ 1·46750; R_C 56·09, R_D 56·38, R_F 57·06, $R_{G'}$ 57·58; $R_{G'-C}$ 1·49, R_{F-C} 0·97; $Mn_D^{20°}$ 253·87. Densities determined: $d_4^{20°}$ 0·8409, $d_4^{62·7°}$ 0·8091, $d_4^{85·7°}$ 0·7904.

17·3°	18·01	17·77	0·8429	28·05	476·0	86·9°	15·11	14·97	0·7895	21·98	478·1
62·2	16·10	15·86	0·8095	24·04	476·9					Mean	477·0

(Mann and Purdie, *loc. cit.*, give b. p. 108—109°/15 mm., $d^{24°}$ 0·8408, $\gamma_{24°}$ 27·60, *P* 474·8.)

19. iso*Amyl sulphide* (Eastman Kodak). B. p. 85·5°/5 mm.; *M* 174·34; n_C 1·45002, n_D 1·45267, n_F 1·45912, $n_{G'}$ 1·46403; R_C 56·18, R_D 56·47, R_F 57·16, $R_{G'}$ 57·68; $R_{G'-C}$ 1·50, R_{F-C} 0·98; $Mn_D^{20°}$ 253·26. Densities determined: $d_4^{20°}$ 0·8340, $d_4^{60·0°}$ 0·8031, $d_4^{85·5°}$ 0·7830, $d_4^{120·3°}$ 0·7567.

Apparatus *B*.

15·2°	13·71	13·47	0·8377	26·46	472·0	87·4°	11·37	11·13	0·7823	20·42	473·7
62·0	12·14	11·90	0·8016	22·37	473·0	121·8	10·20	9·96	0·7555	17·64	473·0
										Mean	472·9

20. n-*Hexyl sulphide.* This was prepared from 69 g. of *n*-hexyl bromide, b. p. 154·5—156°/759 mm. [from *n*-hexyl alcohol, b. p. 156—157°/765 mm. (Carbide and Carbon Chemicals Corporation) by hydrogen bromide–sulphuric acid method], 49 g. of anhydrous sodium sulphide, and 88 c.c. of rectified spirit, and refluxing for 20 hours on the steam-bath (compare **14**). The yield of crude product was 38 g. B. p. 113·5°/4 mm.; *M* 202·39; n_C 1·45596, n_D 1·45856, n_F 1·46492, $n_{G'}$ 1·46965; R_C 65·41, R_D 65·73, R_F 66·51, $R_{G'}$ 67·10; $R_{G'-C}$ 1·69, R_{F-C} 1·10; $Mn_D^{20°}$ 295·21. Densities determined: $d_4^{20°}$ 0·8411, $d_4^{41·0°}$ 0·8264, $d_4^{58·4°}$ 0·8140, $d_4^{85·7°}$ 0·7941.

Apparatus *D*.

t.	*h.*	*H.*	$d^{t°}_{4°}$.	*γ*.	*P*.	*t.*	*h.*	*H.*	$d^{t°}_{4°}$.	*γ*.	*P*.
25·3°	13·78	13·54	0·8373	28·00	556·0	62·3°	12·64	12·40	0·8113	24·84	556·9
28·9	13·65	13·41	0·8348	27·65	555·9	88·7	11·82	11·58	0·7921	22·65	557·4
41·9	13·25	13·01	0·8258	26·53	556·2					Mean	556·5

(Mann and Purdie, *loc. cit.*, give b. p. 136—138°/20 mm., $d^{24°}$ 0·8447, $\gamma_{24°}$ 27·83, *P* 549·2.)

21. n-*Heptyl sulphide*. This was prepared from 60 g. of *n*-heptyl bromide, b. p. 178—179°/762 mm. (from *n*-heptyl alcohol, b. p. 175·5—176·5°/771 mm.; "Organic Syntheses," 1926, **6**, 52, by hydrogen bromide–sulphuric acid method), 39 g. of anhydrous sodium sulphide, 70 c.c. of rectified spirit, and refluxing on the steam-bath for 20 hours. The yield of the crude dry product was 35·5 g. B. p. 141·5°/4·5 mm.; *M* 230·44; n_C 1·45799, n_D 1·46055, n_F 1·46687, $n_{G'}$ 1·47137; R_C 74·72, R_D 75·09, R_F 75·96, $R_{G'}$ 76·59; $R_{G'-C}$ 1·87, R_{F-C} 1·24; $Mn_D^{20°}$ 336·58. Densities determined: $d^{20°}_{4°}$ 0·8416, $d^{41·9°}_{4°}$ 0·8277, $d^{60·6°}_{4°}$ 0·8147, $d^{88·7°}_{4°}$ 0·7968.

20·2°	18·82	18·58	0·8414	29·27	637·0	60·7°	17·30	17·06	0·8146	26·02	638·8
41·4	18·05	17·81	0·8278	27·61	638·1	87·7	16·21	15·97	0·7961	23·81	639·4
										Mean	638·4

(Mann and Purdie, *loc. cit.*, give b. p. 164°/20 mm., $d^{24°}$ 0·8402, $\gamma_{24°}$ 28·61, *P* 633·6.)

22. n-*Octyl sulphide*. This was prepared from 64 g. of *n*-octyl bromide, b.p. 200—200·5°/764 mm. (from *n*-octyl alcohol, b. p. 193—194°/763·5 mm., Deutsche Hydrierwerke Akt., by the same method as **21**), 39 g. of anhydrous sodium sulphide, 70 c.c. of rectified spirit, and refluxing for 20 hours on the steam-bath. The yield of the crude dry product was 39·5 g. B. p. 161·5°/4 mm.; *M* 258·49; n_C 1·45958, n_D 1·46215, n_F 1·46848, $n_{G'}$ 1·47310; R_C 83·75, R_D 84·16, R_F 85·14, $R_{G'}$ 85·86; $R_{G'-C}$ 2·11, R_{F-C} 1·39; $Mn_D^{20°}$ 377·96. Densities determined: $d^{25·0°}_{4°}$ whence $d^{20°}_{4°}$ 0·8447 (extrap.), $d^{41·9°}_{4°}$ 0·8295, $d^{60·6°}_{4°}$ 0·8164, $d^{87·4°}_{4°}$ 0·7977.

Apparatus *D*.

21·7°	14·78	14·54	0·8434	30·28	719·0	61·1°	13·27	13·03	0·8156	26·25	717·3
25·9	14·65	14·41	0·8405	29·91	719·2	87·4	12·50	12·26	0·7977	24·15	718·4
41·3	13·82	13·58	0·8293	27·81	716·0					Mean	718·0

(Mann and Purdie, *loc. cit.*, give b. p. 184—185°/20 mm., $d^{24°}$ 0·8409, $\gamma^{24°}$ 29·10, *P* 713·5.)

23. *Methyl* n-*butyl sulphide*. 23·5 G. of *n*-butylthiol, b. p. 98—98·5°/766 mm. (Eastman Kodak, redistilled), were dropped slowly into 205 c.c. of 10% aqueous sodium hydroxide solution with vigorous stirring which was continued until the liquid was homogeneous. 32·2 G. of methyl sulphate were added during 1 hour. The liquid soon became cloudy and heat was evolved. Stirring was continued for 2 hours at room temperature, and the mixture set aside for 6 hours. The upper layer of sulphide was then removed, washed 4 times with one-quarter of its volume of 10% sodium hydroxide solution, then with water until neutral, and dried with calcium chloride. The yield of the crude dry product was 22·5 g. It was distilled from sodium in a fractionating Claisen flask and a middle fraction collected. B. p. 122·5°/761 mm.; *M* 104·21, n_C 1·44498, n_D 1·44776, n_F 1·45452, $n_{G'}$ 1·45974; R_C 32·92, R_D 33·10, R_F 33·53, $R_{G'}$ 33·94; $R_{G'-C}$ 1·02; R_{F-C} 0·61; $Mn_D^{20°}$ 150·93. Densities determined: $d^{20°}_{4°}$ 0·8427, $d^{40·7°}_{4°}$ 0·8239, $d^{60·6°}_{4°}$ 0·8055, $d^{87·1°}_{4°}$ 0·7809.

21·0°	16·83	16·59	0·8418	26·15	280·1	61·6°	14·74	14·50	0·8046	21·85	280·1
42·1	15·77	15·53	0·8226	23·92	280·3	91·3	13·19	12·95	0·7770	18·84	280·0
										Mean	280·1

24. *Methyl* iso*butyl sulphide*. This was prepared from 24·3 g. of *iso*butylthiol (Eastman Kodak, b. p. 87·5°/764 mm.), 210 c.c. of 10% sodium hydroxide solution, and 33·2 g. of methyl sulphate as under **23**. The yield of crude product was 24 g. B. p. 112·5°/760 mm.; *M* 104·21; n_C 1·44062, n_D 1·44333; n_F 1·45004, $n_{G'}$ 1·45515; R_C 32·99, R_D 33·17, R_F 33·60, $R_{G'}$ 33·93; $R_{G'-C}$ 0·94, R_{F-C} 0·61; $Mn_D^{20°}$ 150·41. Densities determined: $d^{20°}_{4°}$ 0·8335, $d^{42·4°}_{4°}$ 0·8145, $d^{61·2°}_{4°}$ 0·7971, $d^{84·2°}_{4°}$ 0·7757.

20·7°	16·22	15·98	0·8329	24·92	279·6	63·3°	14·17	13·93	0·7953	20·74	279·6
43·4	15·20	14·96	0·8136	22·79	279·9	88·1	12·80	12·56	0·7723	18·16	279·1
										Mean	279·6

25. *Methyl* tert.-*butyl sulphide*. This was prepared from 23 g. of *tert.*-butylthiol (Eastman Kodak, redistilled), b. p. 63—64°/753 mm., 200 c.c. of 10% sodium hydroxide solution, and 31·5 g. of methyl sulphate as under **23**. The yield of crude product was 19·5 g. B. p. 99°/766 mm. (Rheinboldt, Mott, and Motzkus, *loc. cit.*, give b. p. 101—102°); *M* 104·21; n_C 1·43743, n_D 1·44023, n_F 1·44703, $n_{G'}$ 1·45229; R_C 33·10, R_D 33·29, R_F 33·73, $R_{G'}$ 34·08; $R_{G'-C}$ 0·98; R_{F-C} 0·63; $Mn_D^{20°}$ 150·14. Densities determined: $d^{20°}_{4°}$ 0·8257, $d^{40·9°}_{4°}$ 0·8060, $d^{64·5°}_{4°}$ 0·7836.

19·0°	15·48	15·24	0·8266	23·59	277·9	62·8°	13·20	12·96	0·7852	19·05	278·0
41·4	14·34	14·10	0·8055	21·27	277·9					Mean	277·9

26. *Ethyl* n-*butyl sulphide* (Eastman Kodak). B. p. 142·5°/758 mm.; *M* 118·23; n_C 1·44604, n_D 1·44876, n_F 1·45549, $n_{G'}$ 1·46069; R_C 37·68, R_D 37·89, R_F 38·38, $R_{G'}$ 38·75; $R_{G'-C}$ 1·09, R_{F-C} 0·70; $Mn_D^{20°}$ 171·29. Densities determined: $d^{20°}_{4°}$ 0·8367, $d^{41·4°}_{4°}$ 0·8200, $d^{60·2°}_{4°}$ 0·8034.

Apparatus *D*.

18·9°	13·10	12·86	0·8377	26·60	320·5	41·1°	12·23	11·99	0·8202	24·29	320·0
23·5	12·93	12·69	0·8339	26·13	320·5	60·9	11·52	11·28	0·8029	22·37	320·2
										Mean	320·3

27. *Ethyl* tert.-*butyl sulphide*. This was prepared from 17·7 g. of *tert.*-butylthiol, 200 c.c. of 10% sodium hydroxide solution, and 30·3 g. of ethyl sulphate as under **23**. The yield of crude product was 15 g. B. p. 119·5°/761 mm. (Rheinboldt, Mott, and Motzkus, *loc. cit.*, give b. p. 56—57°/109 mm.); *M* 118·23; n_C 1·43890, n_D 1·44164, n_F 1·44844, $n_{G'}$ 1·45356; R_C 37·93, R_D 38·12, R_F 38·63, $R_{G'}$ 39·02; $R_{G'-C}$ 1·09, R_{F-C} 0·70; $Mn_D^{20°}$ 170·44. Densities determined: $d^{20°}_{4°}$ 0·8200, $d^{41·5°}_{4°}$ 0·8021, $d^{60·9°}_{4°}$ 0·7848, $d^{86·7°}_{4°}$ 0·7615.

21·5°	15·48	15·24	0·8187	23·36	317·5	59·6°	13·66	13·42	0·7859	19·75	317·1
43·0	14·52	14·28	0·8006	21·41	317·7	87·5	12·23	11·99	0·7608	17·08	316·6
										Mean	317·2

28. *Phenyl sulphide.* This was prepared from redistilled sulphur monochloride, b. p. 133—134°/750 mm., and sodium-dried " AnalaR " benzene by the Friedel–Crafts reaction (" Organic Syntheses," 1934, **14**, 36); a perfectly colourless and constant-boiling product was obtained. B. p. 145°/8 mm.; *M* 186·26; n_C 1·62575, n_D 1·63343, n_F 1·65375, $n_{G'}$ 1·67158; R_C 59·19, R_D 59·77, R_F 61·29, $R_{G'}$ 62·60; $R_{G'-C}$ 3·41, R_{F-C} 2·10; $Mn_D^{20°}$ 304·24. Densities determined: $d_4^{20°}$ 1·1136, $d_4^{60·1°}$ 1·0823, $d_4^{84·8°}$ 1·0628, $d_4^{120·8°}$ 1·0352.

Apparatus *B*.

t.	*h.*	*H.*	$d_{4°}^{t°}$.	*γ*.	*P.*	*t.*	*h.*	*H.*	$d_{4°}^{t°}$.	*γ*.	*P.*
16·4°	16·49	16·25	1·1164	42·54	426·1	86·4°	14·64	14·40	1·0616	35·85	429·3
61·9	15·27	15·03	1·0809	38·10	428·1	121·6	13·44	13·20	1·0346	32·02	428·3
										Mean	428·0

29. *Phenyl selenide.* This was obtained as a reddish-yellow liquid as described in " Organic Syntheses," 1938, **18**, 27. B. p. 141°/4 mm.; *M* 233·16; n_D 1·65002*; R_D 62·93; $Mn_D^{20°}$ 384·71. Densities determined: $d_4^{20°}$ 1·3515, $d_4^{58·5°}$ 1·3174, $d_4^{88·7°}$ 1·2902, $d_4^{120·7°}$ 1·2628.

Apparatus *B*.

23·5°	13·86	13·62	1·3484	43·07	443·0	88·5°	12·35	12·11	1·2904	36·64	444·6
61·0	13·17	12·93	1·3152	39·88	445·5	121·3	11·50	11·26	1·2623	33·33	443·8
										Mean	444·2

Alkyl Sulphites.—The general method of preparation consisted in placing redistilled thionyl chloride (0·5 mol.) in a 100-c.c. Claisen flask, cooling it in ice, and adding the pure alcohol (0·75 mol.) from a tap-funnel during about 1 hour. Hydrogen chloride was rapidly evolved, and it was necessary to shake the flask vigorously and frequently in order to ensure complete interaction. The mixture was refluxed for 45—75 mins. in order to complete the reaction, and then distilled. *n*-Butyl, *n*-amyl, and *iso*amyl sulphites were distilled under diminished pressure.† The crude sulphite was thoroughly dried with anhydrous sodium sulphate, redistilled, and a middle fraction collected for the physical measurements. The latter were made on the same day as the final distillation, for the sulphites slowly decompose on keeping. The yields were excellent.

The alcohols employed were: A.R. absolute methyl and ethyl alcohol (Burrough), *n*-propyl alcohol, b. p. 96—97°/760 mm. (Bisol), *iso*propyl alcohol, b. p. 82—83°/751 mm. (Bisol), *n*-butyl alcohol, b. p. 116—117°/762 mm. (Bisol), *iso*butyl alcohol, b. p. 106·5—107·5°/766 mm. (Bisol), *n*-amyl alcohol, b. p. 136·5—137·5°/765 mm. (Sharples), and *iso*amyl alcohol, b. p. 129—130°/765 mm. (Sharples, synthetic). All the alcohols were dried over A.R. potassium carbonate before fractionation.

30. *Methyl sulphite.* B. p. 126°/760 mm.; *M* 110·13; n_C 1·40712, n_D 1·40929, n_F 1·41464, $n_{G'}$ 1·41847; R_C 22·36, R_D 22·46, R_F 22·72, $R_{G'}$ 22·90; $R_{G'-C}$ 0·54, R_{F-C} 0·36; $Mn_D^{20°}$ 155·21. Densities determined: $d_4^{20°}$ 1·2129, $d_4^{61·9°}$ 1·1587, $d_4^{87·3°}$ 1·1256.

Apparatus *C*.

17·8°	12·10	11·86	1·2158	34·23	219·1	87·6°	9·77	9·53	1·1252	25·46	219·1
61·9	10·71	10·47	1·1587	28·80	220·0					Mean	219·7

31. *Ethyl sulphite.* B. p. 157°/763 mm.; *M* 138·18; n_C 1·41223, n_D 1·41441, n_F 1·41974, $n_{G'}$ 1·42367; R_C 31·76, R_D 31·91, R_F 32·27, $R_{G'}$ 32·54; $R_{G'-C}$ 0·78, R_{F-C} 0·51; $Mn_D^{20°}$ 195·44. Densities determined: $d_4^{20°}$ 1·0829, $d_4^{41·1°}$ 1·0604, $d_4^{61·0°}$ 1·0396, $d_4^{85·3°}$ 1·0125.

Apparatus *D*.

22·9°	11·21	10·97	1·0798	29·25	297·6	61·0°	10·05	9·81	1·0396	25·19	297·8
29·0	11·03	10·79	1·0733	28·60	297·7	85·9	9·25	9·01	1·0119	22·52	297·5
43·1	10·56	10·32	1·0583	26·97	297·6					Mean	297·6

32. n-*Propyl sulphite.* B. p. 191°/764 mm. (uncorr.); *M* 166·23; n_C 1·42200, n_D 1·42426, n_F 1·42969, $n_{G'}$ 1·43358; R_C 41·09, R_D 41·29, R_F 41·75, $R_{G'}$ 42·08; $R_{G'-C}$ 0·99, R_{F-C} 0·66; $Mn_D^{20°}$ 236·76. Densities determined: $d_4^{20°}$ 1·0280, $d_4^{61·7°}$ 0·9880, $d_4^{85·5°}$ 0·9642, $d_4^{121·5°}$ 0·9269.

18·9°	15·22	14·98	1·0291	28·87	374·4	86·2°	12·72	12·48	0·9635	22·52	375·8
61·9	13·60	13·36	0·9878	24·71	375·2	121·3	11·39	11·15	0·9269	19·35	376·2
										Mean	375·4

33. iso*Propyl sulphite.* B. p. 169·5°/764 (uncorr.); *M* 166·23; n_C 1·41255, n_D 1·41476, n_F 1·42009, $n_{G'}$ 1·42399; R_C 41·15, R_D 41·35, R_F 41·81, $R_{G'}$ 42·15; $R_{G'-C}$ 1·00, R_{F-C} 0·66; $Mn_D^{20°}$ 235·18. Densities determined: $d_4^{20°}$ 1·0064, $d_4^{62·3°}$ 0·9644, $d_4^{86·9°}$ 0·9387, $d_4^{120·8°}$ 0·9015.

18·6°	14·21	13·97	1·0078	26·36	373·8	87·4°	11·63	11·39	0·9383	20·01	374·7
61·5	12·57	12·33	0·9652	22·28	374·2	120·8	10·42	10·18	0·9015	17·18	375·4
										Mean	374·5

34. n-*Butyl sulphite.* B. p. 90·5°/5 mm.; *M* 194·28; n_C 1·42864, n_D 1·43098, n_F 1·43638, $n_{G'}$ 1·44036; R_C 50·26, R_D 50·51, R_F 51·06, $R_{G'}$ 51·47; $R_{G'-C}$ 1·21, R_{F-C} 0·80; $Mn_D^{20°}$ 275·47. Densities determined: $d_4^{20°}$ 0·9957, $d_4^{41·1°}$ 0·9775, $d_4^{60·8°}$ 0·9603, $d_4^{86·6°}$ 0·9381.

Apparatus *D*.

19·0°	11·99	11·75	0·9966	28·92	452·1	42·2°	11·32	11·08	0·9765	26·72	452·5
22·4	11·89	11·65	0·9940	28·60	452·0	62·4	10·78	10·54	0·9589	24·96	452·9
30·5	11·71	11·47	0·9866	27·95	451·7	86·0	10·14	9·90	0·9378	22·93	453·8
										Mean	452·5

35. iso*Butyl sulphite.* B. p. 209°/741 mm.; *M* 194·28; n_C 1·42451, n_D 1·42676, n_F 1·43223, $n_{G'}$ 1·43631; R_C 50·32, R_D 50·56, R_F 51·12, $R_{G'}$ 51·54; $R_{G'-C}$ 1·22, R_{F-C} 0·80; $Mn_D^{20°}$ 277·20. Densities determined: $d_4^{20°}$ 0·9862, $d_4^{61·7°}$ 0·9484, $d_4^{87·5°}$ 0·9225, $d_4^{121·7°}$ 0·8897.

* C line almost coincident with D; F and G′ lines not visible.

† Compare " Organic Syntheses," 1939, **19**, 29, for *n*-butyl sulphite; these details were published after the authors' work was completed in 1937—38.

t.	*h.*	*H.*	$d^{t°}_{4°}$.	*γ.*	*P.*	*t.*	*h.*	*H.*	$d^{t°}_{4°}$.	*γ.*	*P.*
15·2°	15·11	14·87	0·9905	27·58	449·5	87·9°	12·43	12·19	0·9221	21·05	451·3
62·0	13·39	13·15	0·9481	23·35	450·4	122·4	11·17	10·93	0·8891	18·20	451·3
										Mean	450·6

36. n-*Amyl sulphite.* B. p. 111·5°/5 mm.; *M* 222·34; n_C 1·43393, n_D 1·43620, n_F 1·44178, n_G 1·44584; R_C 59·52, R_D 59·80, R_F 60·48, $R_{G'}$ 60·94; $R_{G'-C}$ 1·42, R_{F-C} 0·96; $Mn^{20°}_D$ 319·33. Densities determined: $d^{20°}_4$ 0·9726, $d^{91·5°}_4$ 0·9385, $d^{88·6°}_4$ 0·9160, $d^{120·3°}_4$ 0·8878.

16·0°	16·26	16·02	0·9758	29·27	530·0	87·5°	13·72	13·48	0·9164	23·10	531·9
61·7	14·75	14·51	0·9383	25·49	532·5	122·3	12·55	12·31	0·8862	20·43	533·4
										Mean	532·0

37. iso*Amyl sulphite.* B. p. 98·5°/4 mm.; *M* 222·34; n_C 1·43318, n_D 1·43550, n_F 1·44104, n_G 1·44521; R_C 59·44, R_D 59·71, R_F 60·37, $R_{G'}$ 60·86; $R_{G'-C}$ 1·42, R_{F-C} 0·93; $Mn^{20°}_D$ 319·15. Densities determined: $d^{20°}_4$ 0·9726, $d^{91·9°}_4$ 0·9552, $d^{91·5°}_4$ 0·9381, *d* $0^{85·2°}_4$·9181.

15·5°	15·71	15·47	0·9763	28·28	525·2	62·7°	13·97	13·73	0·9371	24·09	525·6
41·4	14·79	14·55	0·9548	26·01	525·9	87·0	13·14	12·90	0·9166	22·14	526·2
										Mean	525·7

38. *Ethyl ethanesulphonate* (as.-*ethyl sulphite*). Pure silver sulphite (from Johnson and Matthey's silver nitrate, pure recrystallised) was refluxed with colourless ethyl iodide in dry ethereal solution (Biltz and Biltz, "Laboratory Methods of Inorganic Chemistry," 1928, 211; Kurbatow, *Annalen*, 1874, **173**, 7); the resultant ester (poor yield) was purified by repeated fractionation. B. p. 210°/760 mm.; *M* 138·18; n_C 1·41842, n_D 1·42036, n_F 1·42496, $n_{G'}$ 1·42819; R_C 30·15, R_D 30·21, R_F 30·57, $R_{G'}$ 30·77; $R_{G'-C}$ 0·62, R_{F-C} 0·42; $Mn^{20°}_D$ 196·27. Densities determined: $d^{20°}_4$ 1·1560, $d^{62·0°}_4$ 1·1356, $d^{62·5°}_4$ 1·1150, $d^{87·0°}_4$ 1·0906.

19·3°	16·84	16·60	1·1567	35·96	292·5	62·0°	15·43	15·19	1·1155	31·73	294·0
30·1	16·53	16·29	1·1463	34·97	293·0	86·2	14·52	14·28	1·0914	29·18	294·3
41·9	16·14	15·90	1·1357	33·81	293·4					Mean	293·4

(Sugden *et al.* give *P* 295·8.)

Alkyl Sulphates.—Commercial methyl sulphate (B.D.H., 100 g.) was kept over "AnalaR" potassium carbonate for 36 hours and then twice distilled. Ethyl sulphate (B.D.H.), *n*-propyl and *n*-butyl sulphates (Eastman Kodak) were purified as follows. 50 G. were shaken for 10 mins. with 15 c.c. of saturated sodium carbonate solution, the ester layer separated, shaken mechanically for 30 mins. with calcium chloride, filtered, and kept over a large quantity of calcium chloride for 24 hours with occasional shaking. The ester was again filtered into a large excess of "AnalaR" potassium carbonate, kept for 24 hours, and distilled (compare Barkenbus and Owen, *J. Amer. Chem. Soc.*, 1934, **56**, 1024).

39. *Methyl sulphate.* B. p. 187·5°/763 mm.; *M* 126·13; n_C 1·38574, n_D 1·38740, n_F 1·39123, $n_{G'}$ 1·39389; R_C 22·29, R_D 22·38, R_F 22·57, $R_{G'}$ 22·71; $R_{G'-C}$ 0·42, R_{F-C} 0·28; $Mn^{20°}_D$ *n*175·00. Densities determined: $d^{20°}_4$ 1·3283, $d^{43·9°}_4$ 1·3003, $d^{61·8°}_4$ 1·2777, $d^{89·5°}_4$ 1·2478.

15·1°	16·05	15·81	1·3342	39·50	237·0	61·4°	14·44	14·20	1·2782	33·99	238·3
40·6	15·23	14·99	1·3043	36·61	237·3	86·5	13·61	13·37	1·2482	31·25	238·9
										Mean	237·9

(Sugden, Reed, and Wilkins, J., 1925, **127**, 1539, give b. p. 187·5°/769 mm., *P* 238·9; the value for $d^{20°}_4$ extrapolated from their results is 1·3322.)

40. *Ethyl sulphate.* B. p. 75°/5 mm.; *M* 154·18; n_C 1·39861, n_D 1·40037, n_F 1·40457, $n_{G'}$ 1·40756; R_C 31·65, R_D 31·77, R_F 32·07, $R_{G'}$ 32·28; $R_{G'-C}$ 0·63, R_{F-C} 0·42; $Mn^{20°}_D$ 215·81. Densities determined: $d^{23°}_4$ 1·1774, $d^{61·7°}_4$ 1·1350, $d^{89·4°}_4$ 1·1095, $d^{120·9°}_4$ 1·0719.

Apparatus *C*.

14·9°	12·36	12·12	1·1825	34·02	314·9	86·4°	10·48	10·24	1·1095	26·97	316·7
61·9	11·18	10·94	1·1348	29·47	316·6	120·7	9·56	9·32	1·0721	23·72	317·4
										Mean	316·4

[Sugden, Reed, and Wilkins, *loc. cit.*, give b. p. 110°/30 mm., *P* 313·8, $d^{20°}_4$ (extrap.) 1·188; Buehler, Gardner, and Clemens, *J. Org. Chem.*, 1927, **2**, 170, give b. p. 77·8—78·0°/6 mm., *P* 318·4.]

41. n-*Propyl sulphate.* B. p. 94°/5 mm.; *M* 182·23; n_C 1·41144, n_D 1·41336, n_F 1·41788, $n_{G'}$ 1·42104; R_C 40·79, R_D 40·96, R_F 41·35, $R_{G'}$ 41·62; $R_{G'-C}$ 0·83, R_{F-C} 0·56; $Mn^{20°}_D$ 257·56. Densities determined: $d^{20°}_4$ 1·1102, $d^{62·2°}_4$ 1·0683, $d^{87·7°}_4$ 1·0452, $d^{119·9°}_4$ 1·0135.

13·3°	15·89	15·65	1·1167	32·73	390·3	87·0°	13·41	13·17	1·0459	25·79	392·6
61·7	14·26	14·02	1·0695	28·08	392·2	120·1	12·32	12·08	1·0133	22·92	393·4
										Mean	392·2

42. n-*Butyl sulphate.* B. p. 109·5°/4 mm.; *M* 210·28; n_C 1·41929, n_D 1·42126, n_F 1·42597, $n_{G'}$ 1·42936; R_C 50·05, R_D 50·26, R_F 50·74, $R_{G'}$ 51·11; $R_{G'-C}$ 1·06, R_{F-C} 0·69; $Mn^{20°}_D$ 298·87. Densities determined: $d^{20°}_4$ 1·0616, $d^{60·9°}_4$ 1·0227, $d^{88·9°}_4$ 1·0039, $d^{119·5°}_4$ 0·9727.

13·6°	16·14	15·90	1·0673	31·77	467·9	85·5°	13·80	13·56	1·0043	25·50	470·5
62·3	14·49	14·25	1·0214	27·25	470·4	120·6	12·54	12·30	0·9717	22·38	470·7
										Mean	469·9

Trialkyl Orthophosphates.—These were prepared by the action of redistilled phosphorus oxychloride upon the sodium alkoxides as described by Evans, Davies, and Jones (J., 1930, 1310), and were purified by at least two distillations under diminished pressure. The b. p.'s of the alcohols employed are those given under *Alkyl Sulphites*. The agreement of the authors' measurements of the densities and refractive indices with those of Evans, Davies, and Jones (*loc. cit.*) is moderate.

43. *Trimethyl orthophosphate.* B. p. 62°/5 mm.; M 140·08; n_C 1·39452, n_D 1·39630, n_F 1·40049, $n_{G'}$ 1·40154; R_C 27·67, R_D 27·74, R_F 27·99, $R_{G'}$ 28·06; $R_{G'-C}$ 0·39, R_{F-C} 0·32; $Mn_D^{20°}$ 195·59. Densities determined: $d_4^{20°}$ 1·2144, $d_4^{60·9°}$ 1·1722, $d_4^{86·7°}$ 1·1436, $d_4^{119·9°}$ 1·1062.

$t.$	$h.$	$H.$	$d_{4°}^{t°}$	$\gamma.$	$P.$	$t.$	$h.$	$H.$	$d_{4°}^{t°}$	$\gamma.$	$P.$
17·5°	16·86	16·62	1·2152	37·76	285·9	86·9°	14·17	13·93	1·1432	29·82	286·3
60·9	15·22	14·98	1·1722	32·88	286·2	120·7	12·83	12·59	1·1053	26·06	286·3
										Mean	286·2

[Evans, Davies, and Jones, *loc. cit.*, give b. p. 73°/10 mm., $d_4^{25°}$ 1·2052, $d_4^{20°}$ 1·2104 (extrap.), $n_C^{25°}$ 1·3934, $n_D^{25°}$ 1·3950, $n_F^{25°}$ 1·3990; R_C 27·769, R_D 27·869, R_F 28·119.]

44. *Triethyl orthophosphate.* B. p. 75·5°/5 mm.; M 182·16; n_C 1·40343, n_D 1·40533, n_F 1·40983, $n_{G'}$ 1·41308; R_C 41·60, R_D 41·77, R_F 42·18, $R_{G'}$ 42·48; $R_{G'-C}$ 0·88; R_{F-C} 0·58; $Mn_D^{20°}$ 255·19. Densities determined: $d_4^{20°}$ 1·0695, $d_4^{60·9°}$ 1·0301, $d_4^{86·7°}$ 1·0021, $d_4^{120·1°}$ 0·9708.

Apparatus *B*.

18·3°	12·27	12·03	1·0712	30·32	398·7	87·4°	10·26	10·02	1·0014	23·53	400·6
61·7	11·01	10·77	1·0293	25·99	399·6	121·1	9·35	9·11	0·9698	20·72	400·7
										Mean	399·9

[Sugden, Reed, and Wilkins, *loc. cit.*, give b. p. 108°/25 mm., $d_4^{20°}$ 1·0737 (extrap.), P 399·1; Evans, Davies, and Jones, *loc. cit.*, give b. p. 90°/10 mm., $d_4^{25°}$ 1·0637, $d_4^{20°}$ 1·0685 (extrap.), $n_C^{25°}$ 1·4021, $n_D^{25°}$ 1·4039, $n_F^{25°}$ 1·4082; R_C 41·706, R_D 41·870, R_F 42·263.]

45. *Tri*-n-*propyl orthophosphate.* B. p. 107·5°/5 mm.; M 224·24; n_C 1·4148, n_D 1·41646, n_F 1·42120, $n_{G'}$ 1·42467; R_C 55·42, R_D 55·66, R_F 56·21, $R_{G'}$ 56·62; $R_{G'-C}$ 1·20, R_{F-C} 0·79; $Mn_D^{20°}$ 317·63. Densities determined: $d_4^{20°}$ 1·0121, $d_4^{60·9°}$ 0·9743, $d_4^{87·1°}$ 0·9518, $d_4^{120·7°}$ 0·9209.

16·9°	15·78	15·54	1·0149	29·46	516·0	87·6°	13·17	12·93	0·9513	23·04	516·4
63·0	13·98	13·74	0·9735	25·05	515·3	121·8	11·88	11·64	0·9199	20·05	515·8
										Mean	515·9

[Evans, Davies, and Jones, *loc. cit.*, give b. p. 121°/10 mm., $d_4^{25°}$ 1·0023, $d_4^{20°}$ 1·0071 (extrap.), $n_C^{25°}$ 1·4118, $n_D^{25°}$ 1·4136, $n_F^{25°}$ 1·4182; R_C 55·635, R_D 55·849, R_F 56·394.]

46. *Tri*isopropyl *orthophosphate.* B. p. 83·5°/5 mm.; M 224·24; n_C 1·40376, n_D 1·40573, n_F 1·41034, $n_{G'}$ 1·41366; R_C 55·56, R_D 55·79, R_F 56·34, $R_{G'}$ 56·76; $R_{G'-C}$ 1·20, R_{F-C} 0·88; $Mn_D^{20°}$ 315·21. Densities determined: $d_4^{20°}$ 0·9867, $d_{4°}^{62·5°}$ 0·9472, $d_{4°}^{87·5°}$ 0·9237, $d_{4°}^{119·9°}$ 0·8931.

15·3°	14·08	13·84	0·9909	25·68	509·4	87·1°	11·50	11·26	0·9241	19·48	509·8
61·7	12·36	12·12	0·9478	21·51	509·5	120·4	10·45	10·21	0·8926	17·06	510·6
										Mean	509·9

47. *Tri*-n-*butyl orthophosphate.* B. p. 138·5°/6 mm.; M 266·32, n_C 1·42295, n_D 1·42496, n_F 1·42988, $n_{G'}$ 1·43343; R_C 69·44, R_D 69·57, R_F 70·43, $R_{G'}$ 70·93; $R_{G'-C}$ 1·49, R_{F-C} 0·99; $Mn_D^{20°}$ 379·50. Densities determined: $d_4^{20°}$ 0·9766, $d_{4°}^{62·8°}$ 0·9431, $d_4^{87·1°}$ 0·9226, $d_{4°}^{120·5°}$ 0·8941.

16·6°	15·59	15·35	0·9794	28·15	626·3	87·3°	13·20	12·96	0·9224	22·38	628·0
62·1	14·39	14·15	0·9433	24·99	631·3	121·6	12·24	12·00	0·8932	20·07	631·1
										Mean	629·2

[Evans, Davies, and Jones, *loc. cit.*, give b. p. 150°/10 mm., $d_4^{25°}$ 0·9727, $d_4^{20°}$ 0·9774 (extrap.), $n_C^{25°}$ 1·4203, $n_D^{25°}$ 1·4224, $n_F^{25°}$ 1·4274; R_C 69·312, R_D 69·616, R_F 70·336. They state that it is "slightly yellowish, the colour indicating incipient decomposition." Our specimen was perfectly colourless, and its properties did *not* change on distillation under diminished pressure.]

48. *Tri*isobutyl *orthophosphate.* B. p. 117°/5·5 mm.; M 266·32; n_C 1·41729, n_D 1·41931, n_F 1·42416, $n_{G'}$ 1·42775; R_C 69·22, R_D 69·51, R_F 70·22, $R_{G'}$ 70·68; $R_{G'-C}$ 1·52, R_{F-C} 1·00; $Mn_D^{20°}$ 377·99. Densities determined: $d_4^{20°}$ 0·9681, $d_4^{61·2°}$ 0·9324, $d_{4°}^{85·1°}$ 0·9128, $d_{4°}^{120·3°}$ 0·8818.

15·3°	14·93	14·69	0·9721	26·74	623·0	87·3°	12·60	12·36	0·9109	21·08	626·5
61·2	13·48	13·24	0·9329	23·13	626·0	120·6	11·36	11·12	0·8815	18·35	625·3
										Mean	625·2

[Evans, Davies, and Jones, *loc. cit.*, give b. p. 138°/10 mm., $d_4^{25°}$ 0·9617, $d_4^{20°}$ 0·9665 (extrap.), $n_C^{25°}$ 1·4152, $n_D^{25°}$ 1·4173, $n_F^{25°}$; R_C 69·358, R_D 69·666, R_F 70·383.]

49. *Tri*-n-*amyl orthophosphate.* B. p. 167°/5 mm. (through an all-glass apparatus; rubber bungs are slightly attacked); M 308·39; n_C 1·42975, n_D 1·43188, n_F 1·43701, $n_{G'}$ 1·44085; R_C 82·88, R_D 83·24, R_F 84·09, $R_{G'}$ 84·74; $R_{G'-C}$ 1·86, R_{F-C} 1·21; $Mn_D^{20°}$ 441·58. Densities determined: $d_4^{20°}$ 0·9608, $d_{4°}^{62·4°}$ 0·9285, $d_4^{87·0°}$ 0·9083, $d_{4°}^{120·0°}$ 0·8816.

The parachor results were unsatisfactory, the parachor increasing appreciably with rise of temperature. [Evans, Davies, and Jones, *loc. cit.*, give b. p. 225°/50 mm., $d_4^{25°}$ 0·9497, $d_4^{20°}$ 0·9542 (extrap.), $n_C^{25°}$ 1·4262, $n_D^{25°}$ 1·4283, $n_F^{25°}$ 1·4332; R_C 83·209, R_D 83·567, R_F 84·401.]

Acknowledgment is made to D. I. Coome, M.Sc., for the preparation and preliminary measurements upon compounds **12**, **13**, **15**, **31**—**38**, **43**—**47**, and **49**. The authors' thanks are tendered to Eastman Kodak Co. for the supply of the pure thiols, sulphides, and disulphides, and to Imperial Chemical Industries, Ltd., for the liberal grants which have defrayed most of the heavy cost of the research.

Woolwich Polytechnic, London, S.W. 18. [*Received, November 2nd*, 1942.]

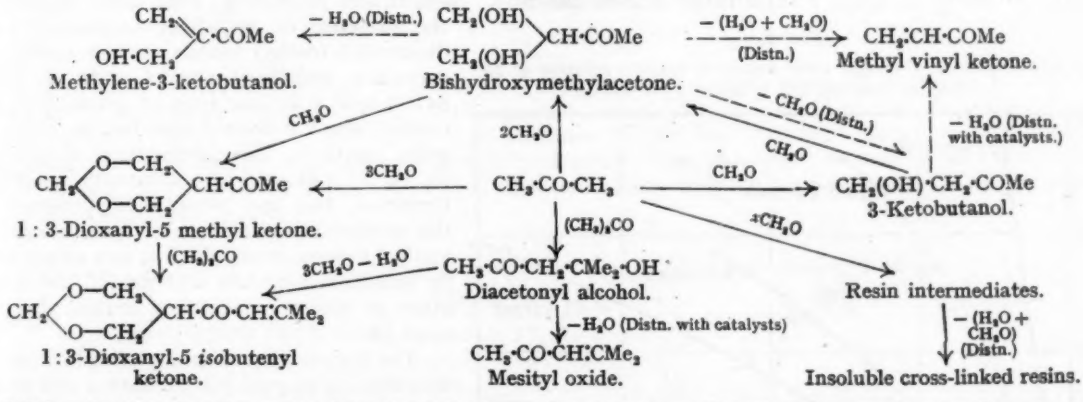
9. *The Preparation and Polymerisation of Methyl Vinyl Ketone.*

By THEODORE WHITE and ROBERT N. HAWARD.

Methyl vinyl ketone is of importance in view of its capacity for polymerisation to a thermoplastic resin. A detailed study has been made of the acetone–formaldehyde condensation with a view to establish the optimum conditions for the production of 3-ketobutanol, from which methyl vinyl ketone is obtained by dehydration. The condensation is complex and its various products are discussed and characterised. The preparation of pure methyl vinyl ketone has been studied, and its rate of polymerisation measured in a series of solvents. Both the high rate of polymerisation obtained in precipitants and the discrepancies observed in the kinetics of the polymerisation in benzene can be explained by the assumption that chain termination is retarded in liquids which do not dissolve the polymer.

THE condensation of acetone and formaldehyde to 3-ketobutanol and the dehydration of the latter to methyl vinyl ketone were first reported by Merling and Köhler (B.P., 1909, 19087; *J. Soc. Chem. Ind.*, **1910**, **29**, 1037). Later work, summarised by Morgan, Megson, and Pepper (*Chem. and Ind.*, **1938**, **57**, 885), established that the condensation was a complex process and, with the present contribution, suggests that the reactions proceeding on condensation and subsequent distillation can be represented as in Fig. 1.

FIG. 1.



Little attention has been given to the isolation and purification of each component or to the manner in which variation of the condensation conditions affects the yield of 3-ketobutanol. It has, however, been claimed by Morgan *et al.* (*loc. cit.*) and Rutovsky, Berlin, and Zabyrina (*J. Gen. Chem. Russia*, 1941, **11**, 550) that 3-ketobutanol enolises to form a terminal methylene group,

$$CH_2(OH)\cdot CH_2\cdot CO\cdot CH_3 \longrightarrow CH_2(OH)\cdot CH_2\cdot C(OH){:}CH_2,$$

and then polymerises under the influence of light or peroxides, a phenomenon not observed with other enols.

The necessity of obtaining pure methyl vinyl ketone before studying its polymerisation led to the present study of the acetone–formaldehyde condensation and to the elucidation of discrepancies in the earlier work. By methods such as those of Fenske, Tonsberg, Quiggle, and Cryder (*Ind. Eng. Chem.*, 1936, **28**, 644; 1937, **29**, 957) and Podbielniak (*Ind. Eng. Chem. Anal.*, **1933**, **5**, 176), the condensation product left after removal of excess of acetone was thoroughly fractionated, thus giving details of the amounts of each component present and providing the products in a very pure state. This gave accurate physical constants for each product and an explanation of the " polymerisation " of 3-ketobutanol.

Earlier workers found that most of the condensation product resinified on distillation. Pressure variation, control of pH, and elimination of oxygen and peroxides did not prevent this, but by distillation in the presence of a high-boiling ester (butyl phthalate) it was found that the volatile components distilled without decomposition and the non-volatile products were precipitated unresinified from the cold ester. High-boiling paraffins did not show this effect, and the reason for the normal occurrence of resinification and its prevention by butyl phthalate remains obscure. The procedure permitted isolation of 70% of the crude product as volatile substances, which were refractionated without decomposition.

Application of this discovery established that a maximum yield of 3-ketobutanol was obtained by refluxing a 4 : 1 molar ratio of acetone : paraformaldehyde at pH 8·3—8·5 for a time just sufficient to permit complete reaction of the paraformaldehyde, the type and effect of variation of the condensation conditions being detailed in the Experimental section.

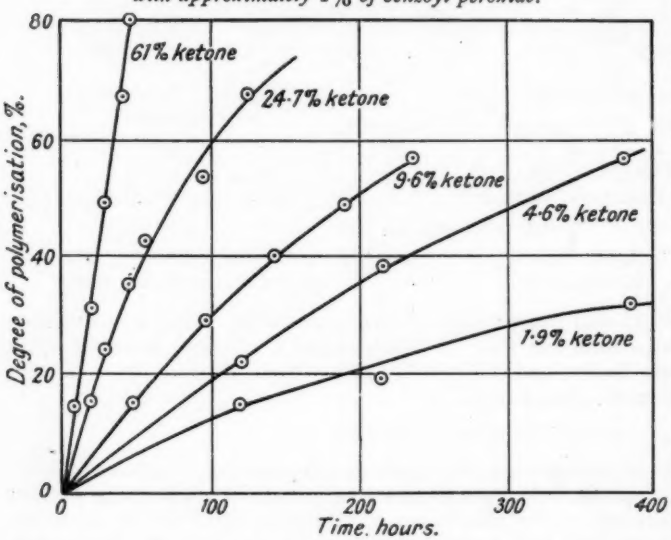
The product obtained under these conditions contained, after removal of the excess of acetone, 30% of non-volatile products, which were not investigated in detail, the volatile portion consisting of: (1) acetone; (2) water (together 9—10%); (3) diacetonyl alcohol, b. p. 63°/12 mm. (4—5%); (4) 3-ketobutanol, b. p. 70—71°/12 mm. (27—28%); (5) methyleneketobutanol, b. p. 82—83°/12 mm. (14—15%); (6) 1 : 3-*dioxanyl*-5 iso*butenyl ketone*, b. p. 90—92°/12 mm. (10—11%); (7) 1 : 3-dioxanyl-5 methyl ketone, b. p. 160°/12 mm. (3—4%).

Fractionation other than by the advanced technique cited gave a main, superficially pure fraction, b. p. 90—92°/12 mm.—the " 3-ketobutanol " of earlier workers. This was found to be a mixture of components (3)—(6), a fact which explains the supposed " polymerisation " of 3-ketobutanol. We have been unable to polymerise pure 3-ketobutanol of b. p. 70—71°/12 mm. and have no evidence of its enolisation. On the other hand, methyleneketobutanol, b. p. 82—83°/12 mm., polymerised with both light and peroxides, and its presence to the extent of some 30% in the mixture of b. p. 90—92°/12 mm. is sufficient to explain the 30% maximum yield of polymer obtained by Rutovsky *et al.* (*loc. cit.*) from their " 3-ketobutanol " and the similar polymerisation recorded by Morgan *et al.* (*loc. cit.*).

Of the components (1)—(7), the occurrence of diacetonyl alcohol and 1 : 3-dioxanyl-5 *iso*butenyl ketone has not previously been noted. The formulation of the latter rests upon analysis and cryoscopic molecular-weight determination (*M*, 165). Bromine absorption showed the presence of one double bond and a molecular weight of 160—170; and the production of acetone on oxidation with alkaline permanganate located this double bond in a terminal *iso*propylidene group. Hydroxylic oxygen was found to be absent, but although, like mesityl oxide and bishydroxymethylacetone, the substance did not give a bisulphite derivative, oxime, or phenylhydrazone, yet the presence of a keto-group was established by the formation of a 2 : 4-dinitrophenylhydrazone. With hot dilute acids formaldehyde was produced, indicating the presence of the remaining two oxygen atoms in a methylenedioxy-group. These facts can be interpreted by more than one formula, but all require the presence in the molecule of a substituted 1 : 3-dioxan ring. Morgan and Holmes (J., 1932, 2667) established the presence of an allied substance, 1 : 3-dioxanyl-5 methyl ketone, in this same condensation, and Morgan and Griffith (J., 1937, 841) found a similar type of product in the methyl ethyl ketone–formaldehyde condensation product. The formulation of product (6) as 1 : 3-dioxanyl-5 *iso*butenyl ketone is tentative, but the established presence in the condensation mixture of 1 : 3-dioxanyl-5 methyl ketone, from which it can easily arise by condensation with acetone (cf. the formation of diacetonylacetone), makes this the most likely of the alternatives.

FIG. 2.

The polymerisation of methyl vinyl ketone in benzene solution at 25° with approximately 1% of benzoyl peroxide.



The preparation of methyl vinyl ketone by dehydration of pure 3-ketobutanol and of the crude condensation mixture was also studied, the results explaining why its b. p.'s have been quoted as 74—87°/760 mm. Dehydration of 3-ketobutanol gave a constant-boiling methyl vinyl ketone–water mixture of b. p. 75°/760 mm. Dehydration of the crude reaction product gave ternary acetone–methyl vinyl ketone–water mixtures, which distilled as pseudo-constant-boiling fractions at any temperature from 69° to 94°/760 mm. according to the type and amount of dehydrating agent used. Refractionation always gave a ternary constant-boiling main fraction, b. p. 73—74°/760 mm., containing 42·5% of acetone, 42·5% of methyl vinyl ketone, and 15% of water, from which pure methyl vinyl ketone, b. p. 81·4°/760 mm. (corr.), $d_{25°}^{25°}$ 0·842, $n^{18°}$ 1·4120, was obtained by adding acetic anhydride to eliminate the water, the resultant acetone–methyl vinyl ketone–acetic acid mixture being readily separated into its pure components by a Fenske column. The methyl vinyl ketone so prepared was used in the following study of its polymerisation.

Polymerisation of Methyl Vinyl Ketone.—The pure ketone polymerised to a solid *d* 1·12, *i.e.*, with a 25% reduction in volume. Such volume changes have frequently been made a measure of the degree of polymerisation (*e.g.*, Bolland, *Proc. Roy. Soc.*, 1941, *A*, **178**, 24), and the method was used throughout this work, consistent results being obtained. The ketone polymerised slowly in the presence of benzoyl peroxide at room temperature and more quickly at 60°. Oxygen appeared to cause an induction period if there was less than 0·1% of peroxide present but the effect was not investigated in detail. The dilatometric method was not convenient for investigation of the undiluted monomer, since the polymer–monomer solution became nearly solid when only 20—30% of the monomer had polymerised, and the following results were all obtained in solvents.

Polymerisation in Benzene.—Polymerisation–time curves for benzene solutions of various concentrations, each containing approximately 1% of catalyst, are given in Fig. 2. For concentrations below 30% the curves are smooth and convex, as if the reactions were following first- or second-order kinetics. Table I illustrates for three concentrations of ketone the result of applying the usual relationships to these curves. The results are remarkable in that, if constancy of the velocity " constant " (k) during any individual reaction is taken as the criterion, the reaction is of first or 3/2 order, whereas if constancy of the velocity " constant " for various

initial concentrations is the criterion, then the result is intermediate between a 3/2 and a second-order reaction. Clearly, the reaction cannot be assigned to any definite order.

TABLE I.

Velocity Constants for the Polymerisation of Methyl Vinyl Ketone in Benzene (first-, 3/2-, and second-order constants).

Ketone, 28·7% by vol. = 3·48 g.-mols./l.; benzoyl peroxide, 0·83% = $3·4 \times 10^{-2}$ g.-mol./l.

Time, hrs.	11.	19.	30.	47.	71.	95.	119.	143.
$10^4 k_1$	41	39	40	40	37	31	33	34
$10^4 k_{3/2}$	26	26	26	28	26	27	26	28
$10^4 k_2$	29	25	30	33	33	36	36	40

Ketone, 9·6% by vol. = 1·14 g.-mols./l.; benzoyl peroxide, 1·0% = $4·1 \times 10^{-2}$ g.-mol./l.

Time, hrs.	24.	48.	72.	96.	120.	144.	168.	192.
$10^4 k_1$	12·5	15	15	16	15	16	15	15
$10^4 k_{3/2}$	16	17	18	19	18	19	19	20
$10^4 k_2$	31	32	34	38	38	40	41	43

Ketone, 1·9% by vol. = 0·23 g.-mol./l.; benzoyl peroxide 0·99% = $4·1 \times 10^{-2}$ g.-mol./l.

Time, hrs.	216.	384.	600.	880.	1,296
$10^4 k_1$	4·3	4·3	4·4	4·2	3·8
$10^4 k_{3/2}$	11	11	13	13	12
$10^4 k_2$	44	53	62	67	71

This point is further emphasised by Table II, which gives a complete series of constants for the range 0·49—36·7% of methyl vinyl ketone (by vol.), the most satisfactory constant for each individual reaction being italicised. The results at the lowest concentrations are the least accurate, since the volume changes measured were very small. The results will not be discussed here, but it may be noted that a similar result was recorded for the polymerisation of vinyl acetate in toluene solution by Cuthbertson, Gee, and Rideal (*Proc. Roy. Soc.*, 1939, *A*, **170**, 315).

TABLE II.

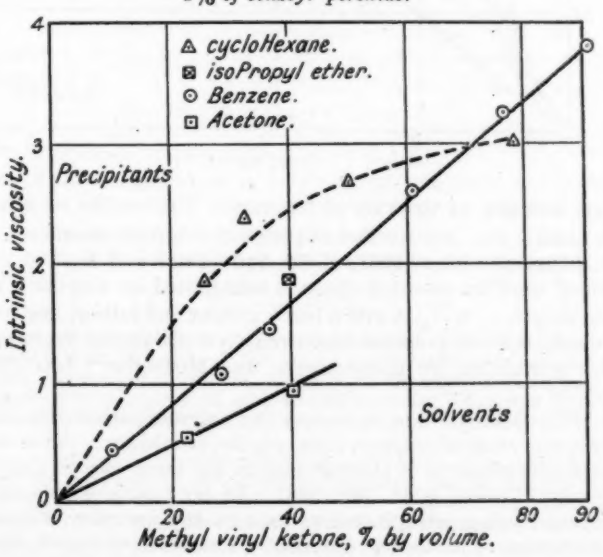
Velocity Constants for the Polymerisation of Methyl Vinyl Ketone in Benzene at 0·49—36·7% by Vol. (0·059—4·4 g.-mol./l.).

Approximately 1% Catalyst throughout.

Concn., g.-mols./l.	0·059.	0·23.	0·55.	1·14.	3·48.	4·4.
$10^4 k_1$	2·8	4·2	*9·0*	*15*	37	40
$10^4 k_{3/2}$	*15*	*12*	16	18	*27*	*29*
$10^4 k_2$	130	60	70	38	40	39

FIG. 3.

Intrinsic viscosity of methyl vinyl ketone polymers formed in various solvents at 25° with approximately 1% of benzoyl peroxide.



Changes in Intrinsic Viscosity.—Fig. 3 depicts the intrinsic viscosities (η_i) (cf. Gee, *Trans. Faraday Soc.*, 1940, **36**, 1167) of methyl vinyl ketone polymers formed in benzene and other solvents in the presence of approx. 1% of benzoyl peroxide. The results show that for benzene solutions the final viscosity is approximately

proportional to the initial concentration of ketone. Hence it may be concluded that this variation in chain length will, of itself, introduce a factor proportional to the concentration of the ketone into any kinetic equation and therefore will raise the order by unity. If the evidence given above were taken as implying a first-order reaction, all the other processes would have to be zero order as far as the ketone concentration is concerned.

TABLE III.

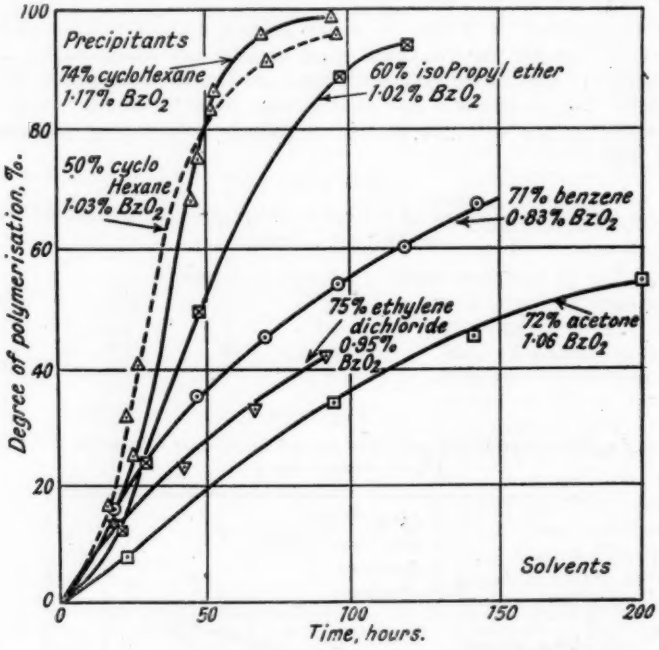
The Effect of Catalyst Concentration on the Polymerisation of Methyl Vinyl Ketone.

Ketone, g.-mols./l.	3·5	3·2	3·5	3·7	3·9
Catalyst (C_0), g.-mol./l.	0·034	0·0145	0·0062	0·0027	0·0013
$10^3 k_1$	3·7	2·1	1·9	1·2	0·92
$10^3 k_1 \times 1/\sqrt{C_0}$	20	18	24	23	26
Intrinsic viscosity	1·08	1·42	1·83	3·0	3·1
Intrinsic viscosity $\times \sqrt{C_0}$	0·20	0·17	0·14	0·16	0·11

The Effect of Catalyst Concentration.—These results suggested that any investigation of the effect of catalyst concentration should be carried out at a single concentration of ketone, whereby the effects due to the uncertain order of the reaction would be largely eliminated. In Table III the first-order constant (k_1) is given, in these

FIG. 4.

Polymerisation of methyl vinyl ketone in various solvents at 25° with approximately 1% of benzoyl peroxide.



circumstances, purely as an estimate of the rate of reaction. The results show that the rate of reaction is proportional to $\sqrt{C_0}$, as is usually the case for these catalysed polymerisations (cf. Cuthbertson *et al.*, *loc. cit.*; Schultz and Husemann, *Z. physikal. Chem.*, 1938, *B*, **39**, 246; Price and Kell, *J. Amer. Chem. Soc.*, 1941, **68**, 798), and it may be concluded that the reaction chain is terminated by a process of mutual saturation. The fact that the product, chain length $\times \sqrt{C_0}$, is much less constant and falls at low concentrations of the catalyst suggests that the reaction chain and the polymer chain may not always be synonymous and that a process of chain transfer such as that postulated by Kamenskaya and Medvedev (*Acta Physicochim.*, 1940, **13**, 565), occurs.

The Effect of Variation of the Solvent.—Fig. 4 depicts the polymerisation of methyl vinyl ketone in a series of solvents; it is obvious that the rates of reaction differ widely, particularly in the later stages. This difference appears to be correlated with precipitation of the polymer in the same way as that observed for methyl methacrylate by Norrish and Smith (*Nature*, 1942, **150**, 336). In both *cyclo*hexane and *iso*propyl ether only the monomer is soluble, the polymer being precipitated as soon as any quantity is formed, whereas both acetone and ethylene dichloride are good solvents for the polymer. Reference to Fig. 3 shows that the solvents which give the highest reaction rates also give the longest chain lengths, but the difference in the rate of reaction is greater than that in molecular weight.

In view of the complex nature of the curves, no attempt has been made to analyse the reaction in *cyclo*hexane or *iso*propyl ether, but the reactions in ethylene dichloride and in acetone appear to give satisfactory

3/2- and second-order constants, respectively, as may be seen in Table IV. No allowance has been made for decomposition of the benzoyl peroxide in any of these reactions. It is certainly slow at 25°, but it could easily be fast enough to affect the kinetics of the longest reactions (50 days). The fact, however, that consistent kinetics are given in ethylene dichloride after this time suggests that the decomposition cannot be large and, in any case, the inconsistencies obtained with benzene cannot be attributed to this cause.

TABLE IV.

Velocity Constants for the Polymerisation of Methyl Vinyl Ketone in Acetone and in Ethylene Dichloride.
[*Constants corrected for small deviations of* C_0 *from* 0·041 *g.-mol./l.* (1%), C_0 *being assumed low.*]

Acetone.

Ketone, g.-mol./l.	1·0	2·7	3·4	4·75
$10^3 k_2$	1·5	2·5	1·9	1·9

Ethylene dichloride.

	Methyl vinyl ketone = 0·16 g.-mol./l.						Methyl vinyl ketone = 3·0 g.-mols./l.			
Time, hrs.	120	316	384	600	888	1296	19	43	67	91
$10^3 k_{3/2}$	2·4	3·0	2·3	2·5	2·5	3·3	3·0	2·0	1·9	2·0

Discussion.—The results in different solvents are in agreement with those of Norrish and Smith (*loc. cit.*) and can be explained on similar lines—that precipitation reduces the rate of chain termination and hence increases the rate of reaction. The fact that the polymer chain length is not equivalently increased shows that the interaction of two active polymer chains plays a more important part in terminating the reaction chains than the polymer chains, *i.e.*, that chain transfer occurs.

This precipitation theory can also be extended to cover the irregularities in the kinetics of polymerisation in benzene, which is a poor solvent for the polymer. Here the accumulation of micellar aggregates may cause a similar rise in the rate of reaction as the polymer is formed and so cause a single reaction to appear of lower order than it really is. The theory would, however, appear to predict that the rate of polymerisation would be faster in a viscous solution of pure polymer than in a pure solvent. To test this, an experiment was made in acetone, since the polymer could not be dissolved in benzene, and it was found that in a 3% solution of polymer of $\eta_{\text{rl}} = 2{\cdot}6$ the rate of reaction was the same as in the pure solvent. An explanation of this apparent discrepancy may be that the increase in viscosity when a small amount of polymer is present in a good solvent does not affect the agitation of the different parts of a single chain, which is the most important factor in the termination process, although it may reduce the rate of diffusion of the centre of gravity of the chain. It seems probable, however, that some factor of the viscosity type does play a part in the reaction owing to the relative ease with which simple monomeric substances polymerise to hard materials with very small internal monomeric concentrations.

Although the kinetics of the polymerisation cannot be ascertained with certainty, it seems probable that a bimolecular reaction takes place in benzene and acetone which can be consistently explained as :

Initiation : $M + \text{Catalyst} \longrightarrow \text{Complex}$

$\text{Complex} + M \longrightarrow \text{Chain} + \text{Catalyst}$

Termination : $P_r^+ + P_s^+ \longrightarrow P_r + P_s$ (dead polymer)

Continuation : $P_r + M \longrightarrow P_{r+1}$; rate $\propto [P^+][M]$

i.e., chain length is proportional to [M].

Together, these give the rate of reaction as proportional to $\sqrt{C_0}[M]^{\frac{3}{2}}$.

The relation of chain length to concentration is, however, an uncertain factor which may account for the 3/2 order in the case of ethylene dichloride. Alternatively, it may be possible for this solvent to play the part of one of the monomer molecules in the initiation mechanism.

The results do not justify more detailed attention to the reaction mechanisms.

EXPERIMENTAL.

Fractionation.—Fractionations were carried out with Fenske columns (*loc. cit.*) and a total-condensation still-head, using a 10/1 reflux ratio and a distillation rate of 1—3 g./min. The column for atmospheric-pressure distillations had an internal diameter of 14 mm. and was packed for 50 cm. with 3 mm. diameter single helices made from 26-gauge nickel wire. Reduced pressure distillations were conducted with a similar type of column of 25 mm. internal diameter packed for 45 cm. with 6 mm. helices. The Podbielniak (*loc. cit.*) type of column was used for comparative purposes and gave identical results.

3-*Ketobutanol.*—3 L. of acetone, 315 g. of paraformaldehyde, and 20 ml. of 2N-methyl-alcoholic potash (pH = 8·3—8·5) were refluxed with mild stirring until 4 drops of the reaction mixture gave no reaction with 2 ml. of Tollens's reagent (*ca.* 5 mins.), indicating complete reaction of the paraformaldehyde. The reaction mixture was then neutralised with 2N-hydrogen chloride in acetone, and the excess of acetone distilled off on a water-bath until the distillation ceased (recovery = 2365 ml.), leaving the crude condensation product (800 g.). 500 Ml. of butyl phthalate were added to this product, and the mixture distilled under reduced pressure, volatile products distilling up to 180°/15 mm. (575 g.). The remaining non-volatile components of the crude product were precipitated when the butyl phthalate residues cooled.

The distillate was fractionated with the specified Fenske column, the third distinct fraction being 3-ketobutanol, b. p. 70—71°/12 mm., $d_{25^\circ}^{25^\circ}$ 1·029, n^{15° 1·435; yield 215 g., 23% (Found : C, 54·2; H, 9·0; OH, 18·9. Calc. for $C_4H_8O_2$: C, 54·5; H, 9·1; OH, 19·3%). It did not polymerise with peroxides or U.V. light or on exposure to ordinary light for

12 months. Contrary to the statement of earlier workers, it boiled without decomposition (b. p. 182°) at 760 mm. It gave a bisulphite derivative, resinified with alkalis, and was dehydrated to methyl vinyl ketone by numerous dehydrating agents.

Composition of the Crude Condensation Product.—Many samples of crude product prepared as above were fractionated thoroughly, only slight variations being noted. A typical 800-g. sample distilled from butyl phthalate gave 225 g. of non-volatile precipitate and 575 g. of volatile products. Fractionation of the latter gave the fractions: (i) b. p. 15—45°/50—20 mm., 80 g. (9—10%), *i.e.*, water and acetone; (ii) b. p. 63°/12 mm., $n^{15°}$ 1·4225, 33 g. (4—5%); (iii) b. p. 70—71°/12 mm., 215 g. (27—28%), 3-ketobutanol (cf. above); (iv) b. p. 82—83°/12 mm., $d_{25°}^{25°}$ 1·06, $n^{15°}$ 1·4675, 110 g. (14—15%); (v) b. p. 90—91°/12 mm., $n^{15°}$ 1·4720, 80 g. (10—11%); (vi) b. p. 160°/12 mm., 25 g. (3—4%).

Fraction (ii) was diacetonyl alcohol, formed by condensation of two acetone molecules; it had b. p. 164°/760 mm., and with acids or iodine gave mesityl oxide, b. p. 129°/760 mm., $n^{15°}$ 1·4435, with the smell of peppermint and other characteristics of this compound. Fraction (iv) consisted of methylene-3-ketobutanol; it absorbed bromine immediately (94% of the theoretical quantity) and had the characteristic properties of an ethylenic ketol, giving a bisulphite derivative and an acetate, b. p. 95°/25 mm., $n^{15°}$ 1·4530, and conformed with the product finally described by Gault and German (*Compt. rend.*, 1936, **203**, 514) as having b. p. 84—88°/13 mm. It polymerised slowly under the influence of light or peroxides to a product of low molecular weight (Found: C, 59·7; H, 8·5; OH, 18·0. Calc. for $C_5H_8O_2$: C, 59·4; H, 8·9; OH, 18·0%). The acetate (bromine absorption = 97% of the theoretical) polymerised similarly but much more slowly. Fraction (v), believed to be 1 : 3-*dioxanyl*-5 iso*butenyl ketone*, gave a 2 : 4-dinitrophenylhydrazone but no oxime or bisulphite derivative. It could not be acetylated. Analysis indicated the empirical formula $C_5H_{4·5}O$, and bromine absorption (one double bond being assumed) a molecular weight of 177 [Found: C, 63·7; H, 8·0; *M* (Rast), 165. $C_9H_{14}O_3$ requires C, 63·5; H, 8·2%; *M*, 170]. Oxidation with cold alkaline permanganate gave acetone (somewhat less than 1 equiv.), identified after distillation from the reaction mixture as its 2 : 4-dinitrophenylhydrazone and estimated by the iodoform reaction. Treatment with hot 2N-hydrochloric acid split off formaldehyde (1 equiv.), estimated as its phloroglucinol condensation product (Morgan and Griffith, *loc. cit.*). The occurrence of this fraction has not been previously noted. Fraction (vi) corresponded in such details as were available with the 1 : 3-dioxanyl-5 methyl ketone described by Morgan *et al.* (*loc. cit.*) and previously designated " a methylene dioxy derivative."

The non-volatile product (Fraction vii), precipitated on cooling the butyl phthalate residues, was isolated by adding an equal volume of ether and filtering off the product, which was washed with ether and dried, giving a pale yellow amorphous powder; yield 225 g. (28—29%). This product resinified on distillation even at 0·0001 mm.; it was soluble in acetone, alcohol, chloroform, and ethyl acetate, but not in ether or light petroleum. Fractional precipitation indicated it to be non-homogeneous, and viscosity determinations on solutions of the material indicated a low average molecular weight. It was not further investigated.

Condensation Conditions and the Yield of 3-Ketobutanol.—The conditions giving a maximum yield of 3-ketobutanol have already been described. The use of different acetone–paraformaldehyde ratios, of other condensation temperatures, pH values, times of condensation, or of gradual addition of the paraformaldehyde, all gave lower yields of 3-ketobutanol due to incomplete condensation or excessive resin intermediate formation according to the factor involved. Paraformaldehyde was preferable to formalin, reagent purity (within normal limits) had little effect, and the alkalis were the best catalysts for the condensation. The adverse effect of varying one factor could not be completely compensated by varying another. Details of all the experiments carried out cannot be given, but Table V gives the results of a number of comparative experiments designed to elucidate the effect of variation of the condensation conditions upon the yield of 3-ketobutanol. All the condensations were carried out with 315 g. of paraformaldehyde and, except where stated, a 4 : 1 molar ratio of acetone : paraformaldehyde—the reactions being conducted at the b. p. of the mixture with 2N-methyl-alcoholic potash as catalyst except where otherwise indicated.

TABLE V.

Illustrating the Effect of Condensation Conditions on the Yield of 3-Ketobutanol.

Molar ratio, $COMe_2/(CH_2O)_n$.	2N-MeOH–KOH, ml.	pH.	Time of condensation (mins.).	Yield, g.	Remarks.
4/1	9	7·5	5	112 *	Incomplete condensation
,,	11	7·8	,,	183	Maximum efficiency at pH 8·3—8·5; higher pH lowers yield by increasing resin intermediate formation
,,	15	8·0	,,	194	
,,	17	8·3	,,	212	
,,	20	8·5	,,	220 *	
,,	22·5	8·8	,,	169	
,,	25	9·2	,,	147	
,,	40	10·0	,,	122 *	
,,	9	7·5	60	86	Compare with 5-min. results marked *
,,	20	8·5	,,	160	
,,	40	10·0	,,	65	
2/1	20	9·3	5	65	pH changes complicate but do not disguise trend of the results
3/1	20	8·9	,,	104	
4/1	20	8·5	,,	215	
7/1	20	8·0	,,	192	
4/1	5 ml. C_5H_5N	—	360	0	No condensation
,,	20 g. $Ca(OH)_2$	7·5	120	180	Complete condensation in both cases
,,	60 g. K_2CO_3	7·5	120	90	

Methyl Vinyl Ketone.—The crude product (800 g.) from a condensation such as that above was heated with 80 g. of concentrated phosphoric acid, the distillate being fractionated through a Fenske column as it was produced; the main fraction distilled at 73—74°/760 mm.; $n^{15°}$ 1·39—1·406; yield 200 g. Refractionation gave back the same product—a ternary acetone–methyl vinyl ketone–water mixture in the ratio 3 : 3 : 1. This was treated with an equal weight of acetic anhydride, kept at room temperature for 24 hours to remove water, and then refractionated, giving sharp acetone, methyl vinyl ketone, and acetic acid fractions. The methyl vinyl ketone so obtained was a colourless, lachrymatory liquid, b. p. 81·4°/760 mm. (corr.), $n^{15°}$ 1·4120, $d_{25°}^{25°}$ 0·842; yield 95 g., *i.e.*, 54% on the 3-ketobutanol in the crude product or 13% overall yield.

Dehydration of pure 3-ketobutanol in the above manner gave a methyl vinyl ketone–water binary mixture, b. p. 75°/760 mm., which again required acetic anhydride treatment before the pure ketone could be isolated. The product, again produced in a 55% yield, was identical with that above. No further purification of this product was possible

nor were any impurities detected. The pure ketone polymerised readily to a hard colourless resin which absorbed water readily to give the soft rubbery polymer generally described.

The Effect of varying the Type and Amount of Dehydrating Agent.—A number of dehydrating agents were used to convert 3-ketobutanol and the crude condensation product into methyl vinyl ketone. Each produced a main fraction with its own characteristic constants, the product in all cases giving the same ternary mixture of b. p. 73—74°/760 mm., $n_D^{15°}$ 1·39—1·4006, on refractionation. Some of the results are listed below, dehydration being combined with fractionation through a Fenske column in each case. For routine work, 10% phosphoric acid was added, since it gave the product closest to that given by refractionation. The yield of ketone varied but slightly with the dehydrating agent used.

Dehydrating agent.	Proportion, %.	B. p. of product.	n_D.	Dehydrating agent.	Proportion, %.	B. p. of product.	n_D.
H_3PO_4	1	89—92°	1·399 —1·3995	HCl	1	70—73°	1·3882—1·4004
,, ...	10	73—74	1·39 —1·4006	HCl + NaCl ...	1 + 7	71—74	1·3901—1·4030
H_3PO_4 + NaCl	1 + 7	72—74·4	1·3998—1·4048	HCl + $CaCl_2$ ...	1 + 7	68—71	1·3825—1·4008
$CaCl_2$	7	92—94	1·3821—1·3954				

Condensation Conditions and the Yield of Methyl Vinyl Ketone.—The yield of ketone varied with the condensation conditions in the same way as did that of 3-ketobutanol, the data below showing the lower yield of product and higher pH required on carrying out the reaction at room temperature instead of at the b. p.—the reaction being carried out with 3 l. of acetone and 315 g. of paraformaldehyde.

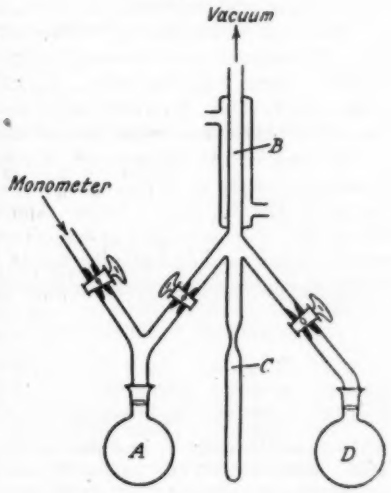
2N-MeOH–KOH, ml.	7·5	12	16	25	30
Yield of ketone, g. { at 25°	incomplete condensation		30	72	60
Yield of ketone, g. { at b. p.	20	78	85	61	57

Technique of investigating the Polymerisation of Methyl Vinyl Ketone.—The monomer was fractionated in nitrogen into flask *A* of the apparatus shown in Fig. 5, samples of b. p. 80·5—82° only being used. Flask *A* was then evacuated, the liquid being allowed to boil freely to carry away any dissolved gases in a stream of vapour. The liquid was then distilled into the condenser *B* so that it ran down into the calibrated tube *C* which already contained a weighed amount of catalyst and in which it could be sealed off. When dilute solutions were being investigated, *C* in some cases took the form of a thermometer with capillary and bulb. Before use, *C* was cleaned with chromic acid, acetone, and distilled water, and dried. Solvents were introduced when necessary from the flask *D*. The charged tube *C* was finally sealed, detached, and then attached to a laminated glass scale and immersed in a thermostat at 25°. Illumination was from behind the scale, and the readings took the form of observation of the downward movement of the meniscus in *C*.

Subsequent work on other monomers showed that the vacuum distillation of the monomer from *A* directly into the reaction tube was the most essential precaution for consistent results.

Solvents.—The solvents used were: Benzene, B.D.H., extra pure for molecular-weight determinations; *cyclo*hexane, B.D.H., spectroscopically pure; acetone, B.D.H., purified by sodium iodide; ethylene dichloride, purified by the method of Proskauer and Weissberger ("Organic Solvents," p. 157), b. p. 81·45—81·55°; *iso*propyl ether, technical, redistilled.

FIG. 5.



The authors express their gratitude to Messrs. Colmore Adhesives Ltd. for permission to publish these results.

COLMORE ADHESIVES LTD., TEAM VALLEY TRADING ESTATE, GATESHEAD-ON-TYNE.

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10. *Dinitrodibenzanthrone.*

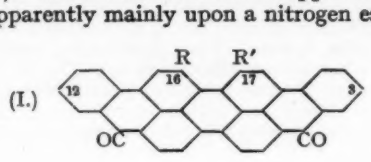
By D. J. BENNETT, R. R. PRITCHARD, and J. L. SIMONSEN.

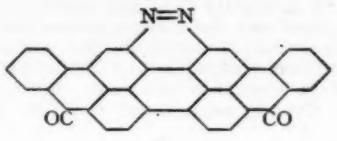
The authors have investigated the structure of dinitrodibenzanthrone and they find that, contrary to the views of Maki, Nagai, and Hayashi (*J. Soc. Chem. Ind. Japan*, 1935, **38**, 710B), the nitro-groups cannot be situated in the 16 : 17-positions. Since on oxidation with chromic acid a *dinitro*-2 : 2′-*dianthraquinonyl*-1 : 1′-*dicarboxylic acid* is obtained, it is suggested that it may be 3 : 12-dinitrodibenzanthrone.

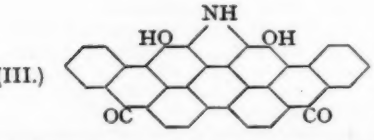
By the nitration of dibenzanthrone in suspension in acetic acid either a mono- or a di-nitrodibenzanthrone or a mixture of these can be prepared depending upon the conditions employed. On reduction with alkaline hydrosulphite the corresponding mono- or di-amines are obtained and it is assumed (Cain and Thorpe, "Synthetic Dyestuffs," 7th Ed., p. 242) that the green dye (Caledon Green B) is an aminodibenzanthrone, yielding a black dye (Caledon Black) when oxidised on the fibre with sodium hypochlorite.

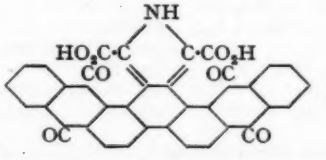
The nitration of dibenzanthrone has been studied in some detail by Maki, Nagai, and Hayashi (*loc. cit.*). They state that from nitrodibenzanthrone a dark blue dye, the monoamine, can be prepared, whereas the diamine, from dinitrodibenzanthrone, gives a green dye. They regard dinitrodibenzanthrone as the 16 : 17-derivative (I; R and R′ = NO_2), and the black dye obtained by oxidation of the diamine (I; R and R′ = NH_2) is considered to be the azine (II). In support of these structures they describe the oxidation of the diamine to a phenol formulated as containing the carbazole ring (III) and finally to a phenanthrapyrroledicarboxylic

acid (IV). No direct evidence in support of these constitutions is advanced and the composition of (IV) was based apparently mainly upon a nitrogen estimation (N, 2·4%).









It has therefore seemed to us desirable to obtain more conclusive evidence for the structure of the dinitrodibenzanthrone and we have examined the products formed by its oxidation with chromic acid. We find the main product to be an acid, from which the *methyl* and the *ethyl* ester were prepared. Although these esters, like the parent acid, are amorphous, their analyses leave no doubt that they are derived from an acid of the composition $C_{30}H_{12}O_{12}N_2$, a *dinitrodianthraquinonyl*-1 : 1′-*dicarboxylic acid*. This assumption was confirmed by the conversion of the nitro-acid into 2 : 2′-dianthraquinonyl-1 : 1′-dicarboxylic acid, the crystalline methyl ester of which decomposed at 374° and appeared to be identical in all respects with a specimen of the methyl ester of the acid obtained by the oxidation of dibenzanthrone.

These experiments show beyond doubt that the nitro-groups in dinitrodibenzanthrone cannot be in the 16 : 17-positions and we would suggest in analogy with other substitution reactions in the benzanthrone series (Cahn, Jones, and Simonsen, J., 1933, 445; Rule and Smith, J., 1937, 1098; Pritchard and Simonsen, J., 1938, 2047; Day, J., 1940, 1474) that they occupy the 3 : 12-positions but we can offer no proof of this. We have not attempted to determine the nature of the Japanese workers' phenol or dicarboxylic acid.

In view of the importance of obtaining for these experiments dibenzanthrone free from *iso*dibenzanthrone it was necessary to devise some method suitable for testing the homogeneity of our material. It was suggested to us by Dr. W. Rogie Angus that the determination of magnetic susceptibility might prove of value. We have used this method and we consider it to be of sufficient promise to warrant a further and thorough trial with similar intractable substances. We wish to express our thanks to Dr. Angus and to Mr. W. K. Hill, M.Sc., for making the measurements recorded below.

Experimental.

3 : 3′-*Dibenzanthronyl*.—This was purified by crystallisation from nitrobenzene and finally from *o*-dichlorobenzene until the magnetic susceptibility ($-0{\cdot}32 \times 10^{-6}$) was constant. The pure substance, decomp. 420°, after sintering at 412—415°, dissolved in sulphuric acid to give a carmine-red solution with an intense red fluorescence.

Dibenzanthrone.—Crude dibenzanthrone, after extraction with pyridine and with water (Soxhlet), was crystallised from cresol, in which it was very sparingly soluble, the apparatus described by Barrett, Dent, and Linstead (J., 1936, 1727) being used. The magnetic susceptibility ($-0{\cdot}540 \times 10^{-6}$) was constant after two crystallisations, remaining unaltered after three further crystallisations.

Dinitrodibenzanthrone.—To a suspension of finely powdered dibenzanthrone (10 g.) in acetic acid (150 c.c.) a solution of nitric acid (*d* 1·48; 60 c.c.) in acetic acid (90 c.c.) was added (mechanical stirring). The temperature of the mixture was raised during 1 hour to 60° and maintained thereat, with stirring, for 12 hours. The cooled mixture was poured into water (500 c.c.), and the solid (10 g.) collected, dried, and dissolved in sulphuric acid (*d* 1·84; 110 c.c.) at 60°, and water (30 c.c.) added with stirring, the temperature being kept below 70°. The dark blue microcrystalline solid (8 g.), which separated from the cooled solution, was collected, washed with sulphuric acid (80%) and then with water until free from mineral acid. After two crystallisations from nitrobenzene the violet solid had a magnetic susceptibility of $-0{\cdot}384 \times 10^{-6}$ (Found: N, 5·3. Calc. for $C_{34}H_{14}O_6N_2$: N, 5·1%). Dinitrodibenzanthrone dissolved in cresol or nitrobenzene to give a dark green solution; its colour in sulphuric acid was reddish-violet. It gave a blue vat having a strong red fluorescence, from which cotton was dyed green.

Dinitro-2 : 2′-*dianthraquinonyl*-1 : 1′-*dicarboxylic Acid*.—Dinitrodibenzanthrone (6 g.) was dissolved in sulphuric acid (*d* 1·84; 90 c.c.), and the cooled solution added gradually, with stirring, to a hot solution (95°) of chromic acid (22·5 g.) in water (675 c.c.). The mixture, well agitated by a current of air, was boiled for 12 hours, a further quantity of chromic acid (7·5 g.) being added after 4 hours. The cooled mixture was diluted with water (*ca.* 2 l.), and the solid, which separated, washed by decantation, collected and dissolved in aqueous ammonia. Acidification of the deep red ammoniacal solution precipitated the nitro-acid as a yellowish-brown solid (1·1 g.). This was best purified by precipitation from its solution in concentrated sulphuric acid (3 times) and solution of the product in warm aqueous ammonia, which removed a brown tar. Acidification of the ammoniacal solution gave the *nitro-acid* as a light brown, amorphous powder (0·5 g.) which did not melt below 400° and was very sparingly soluble in the usual organic media (Found: N, 5·1. $C_{30}H_{12}O_{12}N_2$ requires N, 4·7%). The *methyl* ester, prepared by the addition of an excess of ethereal diazomethane to a suspension of the acid in dioxan, was precipitated by the addition of methyl alcohol to its solution in methyl acetate as a pale yellow powder, blackening at 218° and gradually decomposing above this temperature (Found: C, 61·9; H, 2·7; N, 4·4. $C_{32}H_{16}O_{12}N_2$ requires C, 61·9; H, 2·6; N, 4·5%). The *ethyl* ester, prepared by the action of ethyl alcohol on the acid chloride, separated from alcohol–ethyl acetate as an amorphous orange-brown powder, which sintered at 169—173°, melted at 179—189° and decomposed above 190° (Found: C, 63·3; H, 3·2; N, 4·3. $C_{34}H_{20}O_{12}N_2$ requires C, 62·9; H, 3·1; N, 4·3%).

Methyl 2 : 2′-*Dianthraquinonyl*-1 : 1′-*dicarboxylate*.—(1) *From dibenzanthrone*. Dibenzanthrone (5 g.) was oxidised with chromic acid (22·5 g.) under conditions similar to those used for the oxidation of dinitrodibenzanthrone. The crude acid (1 g.) was a yellowish-brown amorphous powder. For purification, the acid (5 g.) was dissolved in sulphuric acid

(*d* 1·84; 25 c.c.), the solution kept at 100° for 10 minutes and poured into water (500 c.c.) and the pinkish-grey precipitate collected. This was dissolved in aqueous ammonia; the acid (4·3 g.) liberated from the filtered solution by acidification was a yellowish-brown powder. Three repetitions of this process gave a yellow powder (4·1 g.). This was extracted (Soxhlet) with dioxan, which left undissolved a dark tar, and deposited on cooling the nearly pure acid (2 g.) as a light brown powder. This was dissolved in dioxan (150 c.c.), and an excess of an ethereal solution of diazomethane added. After 24 hours in the ice-box, the somewhat sparingly soluble *methyl* ester had separated as a yellow powder (1 g.), decomp. 360—380°. The ester, after two crystallisations from nitrobenzene, was obtained in yellow leaflets, seen under the microscope to consist of characteristic square plates, decomp. 372° (Found: C, 72·7; H, 3·6. $C_{22}H_{18}O_8$ requires C, 72·5; H, 3·4%).

(2) *From dinitro-2 : 2′-dianthraquinonyl-1 : 1′-dicarboxylic acid.* The dinitro-acid (2 g.) in aqueous sodium hydroxide (2%; 150 c.c.) was added gradually with stirring to a suspension of ferrous hydroxide from ferrous sulphate, 15 g., in water, 150 c.c. After digestion for 1 hour, the ferric hydroxide was removed, the deep red filtrate acidified, and the amino-acid, a red amorphous powder, collected. To a solution of the amino-acid (2 g.) in sulphuric acid (*d* 1·84; 35 c.c.) at 20—25° a solution of sodium nitrite (5·3 g.) in sulphuric acid (100 c.c.) was added gradually (mechanical stirring) until a test portion on ice no longer deposited the amino-acid. Stirring was continued for another hour, and the diazonium salt precipitated as a brown powder by the addition of ice. The salt was collected, washed free from mineral acid with water and finally with alcohol, and then refluxed in amyl alcohol with zinc dust for 1·5 hours. The amyl alcohol was removed in steam, and the brown residue extracted with hot aqueous sodium hydroxide (2%). Acidification of the filtered alkaline solution gave the dianthraquinonyl acid as a brown powder. To remove unchanged amino-acid, the crude acid was dissolved in alkali and treated at 0° with potassium permanganate (1%) until an excess was present. This was removed by sulphur dioxide, and the acid (0·6 g.) recovered from the filtered solution. The methyl ester, prepared as described above, crystallised from nitrobenzene in yellow plates, decomp. *ca.* 374°, both alone and in admixture; the ester from two preparations was analysed (Found: C, 72·5, 72·1; H, 3·4, 3·6%).

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11. 1 : 3 : 5 : 7-*Tetranitronaphthalene and the Isomeric Tetranitro-derivatives obtained from* 2 : 6-*Dinitronaphthalene by Nitration.*

By JOSEPH CHATT and W. PALMER WYNNE.

An account is given of the preparation of 2 : 6-dinitronaphthalene from 2 : 6-dihydroxynaphthalene and of the production, isolation and properties of the three tetranitronaphthalenes obtained from the former by nitration. Two of these, the 1 : 3 : 5 : 7- and 1 : 2 : 6 : 8-derivatives, furnish 3 : 5-dinitrobenzoic acid on oxidation and, as an aid in ascertaining the orientation of the nitro-groups in the destroyed rings, use is made of a relation between symmetry and melting point which is found to obtain in typical series of naphthalene di-derivatives containing identical substituents.

ALTHOUGH the dinitronaphthalenes obtained by nitration are the 1 : 8- and 1 : 5-dinitro-, and the trinitronaphthalenes the 1 : 3 : 8- and the 1 : 3 : 5-trinitro-derivatives, the three tetranitronaphthalenes hitherto identified—the 1 : 3 : 5 : 8-; 1 : 3 : 6 : 8-; and 1 : 4 : 5 : 8-isomerides—are exclusively 1 : 8- or *peri*-derivatives. In the second of these, the radicals in each ring occupy respectively the 1 : 3- or *meta*-positions but are so distributed that two of them are also associated in the *peri*-position. It was of interest to ascertain whether the tetranitro-derivative, 1 : 3 : 5 : 7-, in which the *meta*-arrangement holds but the *peri*-association is absent, could be prepared.

Of the methods tried, mention may be made of three. 1 : 3-Dinitronaphthalene (Hodgson and Walker, J., 1933, 1620) was found to be useless as a source, since it furnished 1 : 3 : 8-trinitronaphthalene—a *peri*-derivative—on nitration. And the attempt to prepare the 1 : 3 : 5 : 7-isomeride from diacetyl-1 : 5-diaminonaphthalene failed owing to the sparing solubility of this substance and that of its nitration products in a wide range of solvents, which made isolation and identification impossible. Further, the highly nitrated derivatives were not hydrolysed by acid to give nitro-amines but decomposed, yielding intractable substances.

Thereupon, attention was concentrated on 2 : 6(3 : 7)-dinitronaphthalene, hitherto prepared only from 6-nitro-2-aminonaphthalene in small amount by the diazonium reaction (Veselý and Jakeš, *Bull. Soc. chim.*, 1923, **33**, 942), in view of the probability that with the two ββ-nitro-groups already in place, further substitution would be directed to the more reactive α-positions. And since no instance had as yet been found among the mono-, di- and tri-nitronaphthalenes of the entry of a nitro-group into a position contiguous with that of one already present in the molecule,* there was good reason to expect that the dinitration of this ββ-compound would occur in the desired 4 : 8(1 : 5)-positions which alone were free from that disability.

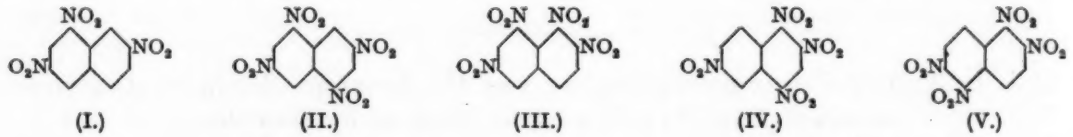
Search for an alternative source of the 2 : 6-dinitro-derivative led to the adoption of 2 : 6-diaminonaphthalene obtained by the amination of 2 : 6-dihydroxynaphthalene by Bucherer's method (*J. pr. Chem.*, 1904, **69**, 47). This diamine, by interaction of its tetrazo-compound with nitrite in the presence of cupro-cupric sulphite (cf. Hantzsch and Blagden, *Ber.*, 1900, **33**, 2554), furnished 2 : 6-dinitronaphthalene in good yield, the final stage leading to the tetra-derivative being completed by dinitration with nitrosulphuric acid. The solid which

* Will's [8-] tetranitronaphthalene is not the 1 : 2 : 5 : 8- but the 1 : 4 : 5 : 8-isomeride (Dimroth and Ruck, *Annalen*, 1925, **446**, 123) and Dhar's claim to have isolated the 1 : 2 : 6 : 8-isomeride is inadmissible, as no evidence is adduced to show that the product was a definite substance or could have the constitution assigned (J., 1920, **117**, 1002).

was removed by filtration from the cold nitration mixture proved to be a single substance (m. p. 260°) and until the precipitate, which separated from the acid filtrate on dilution with much water, was found to contain in addition two isomeric tetranitronaphthalenes (m. p. 138° and 215°) it was regarded as the 1 : 3 : 5 : 7-compound. The total yield of tetranitronaphthalenes obtained from 200 g. of the dinitro-derivative amounted to 149·3 g. or 52·8% of that calculated, the distribution being (i) m. p. 260°, 121·9 g. or 43%; (ii) 138°, 23·8 g. or 8·4%; (iii) m. p. 215°, 3·6 g. or 1·3%. In the final mother-liquors there was also a dark red, highly soluble substance which stained fingers and paper, dissolved with intensification of colour in alkali, and was precipitated from solution in an amorphous condition on acidification: it may have been a polynitronaphthol.

Inasmuch as 1 : 3 : 5 : 7-tetrachloronaphthalene is known (Turner and Wynne, J., 1941, 253), no great difficulty was anticipated in finding out whether, as suggested on p. 33, the tetranitro-derivative, m. p. 260°, has this constitution. But the anticipation proved to be ill-founded, for, although the derived tetramine by octazotisation, followed by interaction of the product with cuprous chloride, gave in the second and third operations, minute yields of a tetrachloronaphthalene which did not depress the m. p., 179°, of the reference compound, yet efforts made some months later failed to repeat these results. Moreover, interaction of the tetranitro-derivative with phosphorus pentachloride—a method applicable to 1 : 5- and 1 : 8-dinitronaphthalene—gave inseparable mixtures of tetra- with penta-chloronaphthalene. And oxidation with dilute nitric acid, which yielded 3 : 5-dinitrobenzoic acid as sole product, ceased to furnish the desired confirmation when it was found that the isomeride, m. p. 138°, under similar conditions gave this acid in addition to its parent, 3 : 5-dinitrophthalic acid.

Of the four ααββ-tetranitro-derivatives obtainable from 2 : 6-dinitronaphthalene—three of them doubtless arising from 1 : 3 : 7-trinitronaphthalene (I) formed as intermediate product—(II) and (III) alone can furnish 3 : 5-dinitro-phthalic or -benzoic acid as an oxidation product and are therefore assignable to the compounds,



(I.) (II.) (III.) (IV.) (V.)

m. p. 260° and 138°. The wide difference between these m. p.'s is thus associated with configurations which differ in respect of symmetry—(II) being centrosymmetrical and (III) asymmetrical.* That this association is not fortuitous is evident when, for example, the ten members of representative series of naphthalene di-derivatives of the type $C_{10}H_6R_2$ are grouped with their respective m. p.'s under the three headings (A) those without symmetry, (B) those with a plane of symmetry, (C) those having a centre of symmetry.

With few exceptions, italicised in the table—the most noteworthy of which being those found among the highly polar dihydroxynaphthalenes—it can be seen that none of the m. p.'s in (B) is lower than any of the four

Melting Points of Naphthalene Di-derivatives (X = $C_{10}H_6$).

		XCl_2.	XBr_2.	XMe_2.	$X(NO_2)_2$.	$X(NH_2)_2$.	$X(NHAc)_2$.	$X(OH)_2$.	$X(OAc)_2$.	$X(CN)_2$.	$X(CO_2Me)_2$
A	1 : 2	35°	68°	oil	158°	98°	234°	103° *	105°	190°	85°
	1 : 3	61	64	oil	145	96	263	124	56	179	—
	1 : 6	49	61	oil	162	86	257	137	73	211	98
	1 : 7	64	75	oil	156	118	213	178	108	167	90
B	1 : 4	68	83	6	*132*	120	304	*176*	129	*208*	*67*
	1 : 8	88	109	63	173	*67*	—	*140*	148	232	104
	2 : 3	120	140	104	171	194	*247*	*161*	—	251	*47*
	2 : 7	114	141	97	234	166	*254*	190	136	267	135
C	1 : 5	107	131	80	216	190	360	265	160	263	119
	2 : 6	135	158	111	279	216	†	222	175	293	186

* Fieser and Hartwell (*J. Amer. Chem. Soc.*, 1935, **57**, 1485).
† Obtained by Friedländer and Lucht (*Ber.*, 1893, **26**, 3033) but m. p. not recorded.

in (A) and that throughout with only one exception, itself also centrosymmetrical, the 2 : 6-compound in each series has the highest m. p. If among tetranitro-derivatives a corresponding relationship between symmetry and m. p. may be assumed, the assignment of (II) to the compound of the higher m. p. 260° becomes inevitable.

Support for this view, but again lacking absolute proof, is furnished by the crystallographic examination of the three tetranitronaphthalenes, m. p. 260°, 215° and 138°. For that of the first two we are indebted to Miss M. J. Boyes-Watson and for the third to Miss E. M. Davidson of the Crystallographic Laboratory. From their reports, it is clear that, whereas the molecule of the isomeride, m. p. 260°, is most probably centrosymmetrical, that of each of the others is of the lowest possible symmetry. As this evidence excludes (V), which is centro-symmetrical, from consideration, (IV) may be tentatively assigned to the isomeride, m. p. 215°.

* The reference here is to the two-dimensional symmetry of the structural formulæ as usually written and not to the symmetry of the molecules represented by those formulæ.

X-Ray data.	M. p. 260°.	M. p. 138°.	M. p. 215°.
Symmetry	Orthorhombic—pseudocubic bipyramids	Monoclinic	Orthorhombic—plate-like crystals
Cell size	$a = 10{\cdot}3$ A. $b = 11$ A. $c = 10$ A.	$a = 27{\cdot}50$ A. $b = 9{\cdot}63$ A.; $\beta = 93°$ $c = 17{\cdot}1$ A.	$a = 10{\cdot}3$ A. $b = 12{\cdot}3$ A. $c = 18{\cdot}0$ A.
Axial ratio	$a : b : c = 0{\cdot}934 : 1 : 0{\cdot}909$	$a : b : c = 2{\cdot}86 : 1 : 1{\cdot}78$	$a : b : c = 0{\cdot}833 : 1 : 1{\cdot}46$
No. of molecules per unit cell	4	16	8
Space group	P bcm	$P 2_1/a$	P cab

M. p. 260°. Since there are 4 molecules per cell, they must occupy special positions in the unit cell and probably lie on centres of symmetry. The molecule seems to be centrosymmetrical.

M. p. 138°. There is every indication from *X*-ray and optical data that the molecules lie in the *a c* plane, giving a layer lattice. There is no sign whatever that the molecules possess any symmetry.

M. p. 215°. Since there are 8 molecules per cell, they must occupy general positions in the unit cell. The molecule seems to be asymmetrical.

In the light of these relationships and of such chemical evidence as has been forthcoming, we see no reason to doubt that the tetranitronaphthalene, m. p. 260°, is the 1 : 3 : 5 : 7-derivative we set out to prepare.

The directive influence of the ββ-radicals on the positions assumed by the entering α-nitro-groups in the production of (II) would seem to be exerted in accordance with the first of two well-defined " laws " of substitution in the naphthalene series, *viz.*, inhibition of entry into any position contiguous with one already occupied by an α- or β-nitro-group already present. But in that of (III), the second " law " would seem to be operative, *viz.*, predilection for entry into the *peri*-position relatively to an α-nitro-group already present. If the yields of (II) and (III) afford evidence of the relative strength of these directive influences, that of " inhibition " is predominant in the dinitration of 2 : 6-dinitronaphthalene.

Experimental.

1 : 3-Dinitronaphthalene, when oxidised with dilute nitric acid (*d* 1·16) at 200°, gave as sole product 3 : 5-dinitrobenzoic acid, m. p. 203°, which did not depress the m. p. of an authentic specimen (Found : C, 39·7; H, 2·1; N, 13·7. Calc. for $C_7H_4O_6N_2$: C, 39·6; H, 1·9; N, 13·2%). Its isolation in place of the expected 3 : 5-dinitrophthalic acid is to be ascribed to the well-known loosening effect of *ortho-para*-nitro-groups, which in this case led to the elimination of the 2-carboxyl radical. Nitration with a 67% excess of nitrosulphuric acid converted 1 : 3-dinitronaphthalene (3 g.), suspended in sulphuric acid (30 g.), into the 1 : 3 : 8-trinitro-derivative (1·5 g.), which, crystallised from acetone, had m. p. 216—220°.

2 : 6-Dihydroxynaphthalene was obtained in the first instance from Schäffer acid (2-naphthol-6-sulphonic acid) by fusion with caustic potash. Later, we were indebted to Messrs. Imperial Chemical Industries (Dyestuffs) Ltd. for a generous supply of the substance which greatly facilitated the progress of the investigation. Before use, the pale brown powder, m. p. 208—210°, was converted into the diacetyl derivative, m. p. 173°, and this in turn hydrolysed by dilute alkali in a nitrogen atmosphere, a colourless product being obtained which crystallised from water in large, thin scales, m. p. 222° (in a vacuum). For conversion into the diamino-compound, 20 g. were heated in a rotating autoclave at 140° during 6 hours, with 400 c.c. of 40% ammonium sulphite solution mixed with 260 c.c. of 20% aqueous ammonia, the solid product being washed first with water, then with 100 c.c. of 5% caustic soda solution, and again with water. Next, suspended in hot water, it was dissolved by adding hydrochloric acid, the solution being made acid to brilliant-green as indicator, then decolourised by animal charcoal, and the base precipitated by the minimum of caustic soda solution. It crystallised from a 50% aqueous pyridine solution in microscopic needles, m. p. (in a vacuum) 217—219°. The yield amounted to 16 g. Addition of hydrochloric acid in excess (40 c.c.) to the decolourised solution precipitated the dihydrochloride in beautiful needles (Found : N, 12·1. Calc. for $C_{10}H_{10}N_2.2HCl$: N, 12·1%).

From the diaminonaphthalene, the 2 : 6-dinitro-compound was prepared by a method based on that by which Hantzsch and Blagden obtained 2-nitro- from 2-amino-naphthalene (*loc. cit.*). First, the diamine (20 g.) in fine powder was dusted into concentrated sulphuric acid (100 g.) and vigorously stirred until all was dissolved at 20—30°. Solid nitrosylsulphuric acid (40 g.), previously washed free from liquid by acetic acid, was then added in one quantity at 15° and, when it had dissolved, acetic acid (140 c.c.) was added slowly at 25—30°, stirring being continued during ½ hour at this temperature. A test sample when added to a little ice should then give a clear solution and show excess of nitrous acid with starch–iodide paper. From the solution, cooled at 5° and vigorously stirred, the tetrazonium compound was precipitated by alcohol (600 c.c.), added very slowly, particularly at first, to prevent the temperature from rising above 20°. Left in the ice-bath until precipitation was complete, the product collected on a filter and washed with alcohol was light brown, but in water rapidly became dark. Its conversion into the dinitro-derivative was effected by suspending finely ground cuprocupric sulphite (80 g.) in a solution of sodium nitrite (400 g.) in water (2 l.) and adding with vigorous stirring the tetrazonium compound freshly dissolved in water. After the rapid evolution of nitrogen had ceased, the whole was warmed on the steam-bath, filtered, washed, and the residue warmed with 2% sulphuric acid until nitrous fumes were no longer observed. Collected on a filter, the red residue, washed finally with alcohol and dried in a desiccator, was ground to a fine powder and sublimed at 230° rising to 270° under 15 mm. The yellow sublimate was crystallised from acetic anhydride; it formed long yellow needles, m. p. 279°, the yield amounting to 10—12 g., whereas Veselý and Jakeš describe it as forming orange-red serrated scales, m. p. 268° (Found : C, 55·5; H, 3·0; N, 13·1. Calc. for $C_{10}H_4O_4N_2$: C, 55·0; H, 3·0; N, 12·9%).

(i) 1 : 3 : 5 : 7-*Tetranitronaphthalene* was obtained by stirring finely powdered 2 : 6-dinitronaphthalene (20 g.) into concentrated sulphuric acid (300 c.c.) at 10°, then adding to the suspension fuming nitric acid (100 c.c.) at such a rate that this temperature was not exceeded, and leaving the mixture overnight. Gradually warmed to 80° in the course of ½ hour and maintained at that temperature for a similar period, the product, rendered ice-cold, was collected on a sintered funnel, washed with concentrated sulphuric acid, then with water and finally with alcohol. From acetic anhydride, it formed orange-yellow, orthorhombic, pseudocubic bi-pyramids, sparingly soluble in the usual solvents, m. p. 260° with decomposition at 263—265° in sealed or open capillary tube (Found : C, 39·1; H, 1·5; N, 18·7. Calc. for $C_{10}H_4O_8N_4$: C, 39·0; H, 1·3; N, 18·2%). The yield amounted to 9·6 g. On oxidation with dilute nitric acid (*d* 1·16) at 200°, it gave a product from which 3 : 5-dinitrobenzoic acid, m. p. 203°, which did not depress the m. p. of an authentic specimen, was the only substance isolated (Found : C, 39·6; H, 2·2; N, 13·4%).

The product obtained by heating it (1·2 g.) with phosphorus pentachloride (4 g.) and oxychloride (4 c.c.) at 180—200° during 15—30 minutes gave on distillation with steam a chloro-derivative (0·23 g.) crystallising from alcohol in slender needles, m. p. 133—134°, which on analysis proved to be a mixture of tetra- with penta-chloronaphthalene in varying proportion—in one case the Cl found was as high as 57·2%—but inseparable either by fractional crystallisation or fractional distillation with steam.*

1 : 3 : 5 : 7-*Tetra-aminonaphthalene.*—When the finely ground tetranitro-compound (5 g.) was washed by alcoholic hydrogen chloride (10 c.c.) into a warm solution of stannous chloride (60 g.) in the same solvent (60 c.c.), vigorous action occurred, which was completed by heating the mixture on a steam-bath for ½ hour. After the solid product, dissolved in hot water (100 c.c.), had been freed from tin by means of an excess of 30% caustic soda solution, the precipitated amine (2·8 g.) forming yellow crystals was washed with water and dried in a vacuum desiccator. It was only sparingly soluble in most solvents, best in hot aqueous pyridine, and in solution rapidly became black owing to oxidation. The tetrahydrochloride formed colourless needles (Found: C, 36·1; H, 5·1; N,1 6·6; Cl, 42·2. Calc. for $C_{10}H_{12}N_4$,4HCl: C, 35·9; H, 4·8; N, 16·8; Cl, 42·5%).

For conversion of the tetramine into tetrachloronaphthalene, Schoutissen's method (*J. Amer. Chem. Soc.*, 1933, **55**, 4535) was followed in the main, the octazotisation being effected by dissolving the hydrochloride (2 g.) in syrupy orthophosphoric acid (*d* 1·75; 70 c.c.), adding concentrated sulphuric acid (6 c.c.) to the solution cooled in a freezing mixture, and then, slowly, at −5° a solution of sodium nitrite (2·5 g.) in concentrated sulphuric acid (14 c.c.) with continuous stirring. On completion of the addition, the temperature was allowed to rise to 15—20° and ½ hour later the reddish mixture was tested for excess of nitrite, which should be present in small amount. Urea (2·5 g.), finely powdered, was then dusted in and, when all effervescence had ceased, the solution was slowly added to a well-stirred solution of cuprous chloride (5·2 g.) in concentrated hydrochloric acid (90 c.c.) cooled in ice, the reaction being completed by raising the temperature slowly to 30° and later to the boiling point. After filtration, the residue, rendered alkaline with caustic soda and distilled with steam, furnished a product (*ca.* 3 mg.) which crystallised from aqueous alcohol in very slender needles, m. p. 178—181°, and when ground with an authentic specimen of 1 : 3 : 5 : 7-tetrachloronaphthalene, gave a mixture which fused at 177—180°, solidified at 177° and then melted at 177—180°.

On repetition of the process, a slightly larger yield of the product was obtained (*ca.* 5·5 mg.) which on analysis gave Cl, 54·1% (Calc. for $C_{10}H_4Cl_4$: Cl, 53·4%). But five attempts to confirm these results, made some months later when corroboration of the constitution had been sought in vain by other methods (p. 34), furnished products (3—5, but in one case 10 mg.) the m. p.'s of which were successively 146°, 138°, 148°, 141°, and 145°, raised by 10—15° after admixture with equal weights of 1 : 3 : 5 : 7-tetrachloronaphthalene. It would therefore seem that the earlier results must have depended on some small manipulative detail which later was overlooked.

The precipitate obtained by pouring the acid filtrates and washings collected from the dinitration of 2 : 6-dinitronaphthalene (200 g.) was pale yellow when dry (81 g.). On extraction with boiling acetone (700 c.c.), a grey residue was left (11·6 g.) sparingly soluble in the ordinary solvents but easily in boiling nitrobenzene, from which almost the whole (10·1 g.) separated on cooling in crystals (m. p. 259°) characteristic of 1 : 3 : 5 : 7-tetranitronaphthalene.

From the hot acetone solution, on the addition of sufficient hot water to induce faint opalescence, a separation in very small scales, m. p. 141—180°, was obtained (17·9 g.) which except for a small amount, m. p. *ca.* 207°, was soluble in benzene and cystallised therefrom in short brittle needles (m. p. 116—120°). Further addition of water to the acetone filtrate gave an ill-defined, pale red separation, m. p. 155—168° (31·5 g.), the red filtrate from which, after removal of the acetone by distillation, deposited an oil solidifying over-night to a red, microcrystalline solid (6·8 g.). By fractional crystallisation of these separations, mainly by the aid of acetic anhydride, acetic acid, benzene–ligroin or nitrobenzene, it proved possible to isolate a further amount of the 1 : 3 : 5 : 7-isomeride (15·8 g., making 25·9 g. in all); a second tetranitronaphthalene, m. p. 138° (23·8 g.), more soluble in most solvents than the foregoing; and a third (3·6 g.), the most soluble of all, which crystallised from alcohol in very pale yellow, four-sided tablets, m. p. 215°. Unexpectedly, the 1 : 3 : 5 : 7-isomeride was found in each of the main fractions and its complete separation from the third, m. p. 215°, proved particularly troublesome.

(ii) 1 : 2 : 6 : 8-Tetranitronaphthalene, m. p. 138°, is more soluble in benzene than its isomerides and crystallises therefrom or from benzene–ligroin with 1 mol. of "benzene of crystallisation" in clusters of needles, m. p. 92°, which is lost on exposure to the air (Found: C_6H_6, 20·5. Calc. for $C_{10}H_4O_8N_4$,C_6H_6: C_6H_6, 20·2%). It is moderately soluble in the ordinary solvents, crystallises from acetic anhydride in pale brown, monoclinic needles, frequently twinned, and dissolves only very sparingly in petrol or chloroform (Found: C, 39·2; H, 1·4; N, 18·2. Calc. for $C_{10}H_4O_8N_4$: C, 39·0; H, 1·3; N, 18·2%). When cooled below its m. p., it solidifies as a clear glass, unless while still fused it is sown at *ca.* 90—100° with a crystal, and it does not begin to decompose below 230°.

On oxidation with dilute nitric acid (*d* 1·16) at 190—200°, it gave a product from which both 3 : 5-dinitrophthalic acid, m. p. 226° (Found: C, 37·9; H, 1·9; N, 10·9. Calc. for $C_8H_4O_8N_2$: C, 37·5; H, 1·6; N, 10·9%), and 3 : 5-dinitrobenzoic acid, m. p. 201—202° (Found: N, 13·7. Calc. for $C_7H_4O_6N_2$: N, 13·2%), were isolated, the latter of which did not depress the m. p. of an authentic specimen. When heated with phosphorus pentachloride (4 g.) and some oxychloride (4 c.c.) at 180° during 20 minutes, it gave a product (1·2 g.) which on distillation with steam yielded a chloro-derivative, m. p. 125—127° (Found: Cl, 50·6. Calc. for $C_{10}H_4Cl_4$: Cl, 53·4%), too small in amount to be recrystallised for comparison with 1 : 2 : 8 : (?)-tetrachloronaphthalene, m. p. 131° (Turner and Wynne, *loc. cit.*).

(iii) Tetranitronaphthalene (m. p. 215°) is the most soluble of the isomerides in the ordinary solvents. It crystallises from acetic anhydride in pale yellow, orthorhombic plates and in either an open or a sealed capillary tube decomposes vigorously at the moment of fusion (Found: C, 39·2; H, 1·8; N, 18·2. Calc. for $C_{10}H_4O_8N_4$: C, 39·0; H, 1·3; N, 18·2%). Mixed with an equal amount of the 1 : 3 : 5 : 7-isomeride, it begins to decompose rapidly at 202°, about one half undergoing fusion at this temperature and the remainder below 230°, and on refusion after solidification has m. p. 230—232°, accompanied by decomposition. The small amount available made further investigation impossible.

Our thanks are due to Dr. M. F. Perutz for helpful discussion of the crystallographic data and to Messrs. G. R. Purdy and R. E. Maxim of this laboratory for the analyses. One of us (J. C.) thanks the Department of Scientific and Industrial Research for a Senior Research Award which made collaboration possible during the session 1940—41.

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* Fractional sulphonation could not be employed, since 1 : 3 : 5 : 7-tetrachloronaphthalene does not undergo sulphonation when shaken in light petroleum solution (b. p. 80—100°) at 100° during 3 hours with chlorosulphonic acid or with 10 or 20% oleum. With the oleum much charring occurred.

12. *The Mechanism of the Oxidation of Oleic and Elaidic Acids and their Methyl Esters by Hydrogen Peroxide in Acetic Acid. Further Observations on the Configurations of the* 9 : 10-*Dihydroxystearic Acids.*

By George King.

The oxidation of oleic acid by hydrogen peroxide in acetic acid at room temperature affords mainly a mixture of monoacetyl derivatives of the dihydroxystearic acid, m. p. 95°. Elaidic acid, however, furnishes an appreciable yield of oxidostearic acid, m. p. 55·5°, in addition to monoacetyl derivatives of the dihydroxystearic acid, m. p. 132°. The methyl esters of oleic and elaidic acids behave similarly, and in all cases small amounts of peroxides, probably of the type CHR(OH)·O·O·CHR·OH, are formed.

r-Oxidostearic acid, m. p. 59·5° (oleic acid epoxide), unites with acetic acid during a few days at room temperature to give the same mixture of 9 : 10-hydroxyacetoxystearic acids (m. p. 81° after purification) as that obtained by oxidation of oleic acid in acetic acid solution. Under similar conditions *r*-oxidostearic acid, m. p. 55·5° (elaidic acid epoxide), is only partly transformed by acetic acid into monoacetyl derivatives of the dihydroxystearic acid, m. p. 132°, nearly 50% remaining unchanged after 11 days.

The oxidostearic acids are considered to be primary products in the oxidation of oleic and elaidic acids by " peracetic acid," and the ultimate formation of the dihydroxystearic acids, m. p.'s 95° and 132° respectively, or their derivatives is ascribed to inversion on fission of the oxide ring.

It was shown by Hilditch (J., 1926, 1829) that oleic and elaidic acids and their methyl esters are oxidised by hydrogen peroxide in the presence of acetic acid to products which, on saponification, furnish the 9 : 10-dihydroxystearic acids, m. p.'s 95° and 132° respectively, in good yields. The same dihydroxy-acids result from the action of perbenzoic acid, which is known to oxidise oleic and elaidic acids in ethereal solution at 0° primarily to the 9 : 10-oxidostearic acids melting respectively at 59·5° and 55·5° (Pigulevski and Petrova, *J. Russ. Phys. Chem. Soc.*, 1926, **58**, 1062; Böeseken and Belinfante, *Rec. Trav. chim.*, 1926, **45**, 918). Conversely, the oxidation of oleic and elaidic acids by potassium permanganate in cold alkaline solution furnishes the isomeric dihydroxy-acids, m. p.'s 132° and 95° respectively (Saytzeff, *J. pr. Chem.*, 1886, **33**, 300; Robinson and Robinson, J., 1925, **127**, 175; Lapworth and Mottram, *ibid.*, p. 1628).

The inversion of configuration which necessarily occurs during one or other of these processes has given rise to some conflict of opinion (Hilditch, *loc. cit.*; Hilditch and Lea, J., 1928, 1576; Pigulevski and Petrova, *loc. cit.*; Böeseken and Belinfante, *loc. cit.*, p. 917). Evidence has been adduced in support of the hypothesis that inversion occurs during hydrolysis of the oxide ring (Esafov, *J. Gen. Chem. Russia*, 1937, **7**, 1403; King, J., 1942, 387), similar examples of which are to be found in the alicyclic series (van Loon, *Chem. Zentr.*, 1920, I, 332; Farmer and Sundralingam, J., 1942, 135). Hilditch and Lea (*loc. cit.*) investigated the action of hydrogen peroxide on the methyl esters of oleic and elaidic acids in acetic acid solution, but were unable to obtain any evidence of the formation of intermediate oxido-compounds. On the other hand, Arbusov and Michailov (*J. pr. Chem.*, 1930, **127**, 1, 92), working more particularly on olefinic compounds of the alicyclic and terpene series, have since shown that peracetic acid resembles perbenzoic in forming cyclic oxides primarily at low temperatures (see also Böeseken and Schneider, *J. pr. Chem.*, 1931, **131**, 285; cf. Böeseken, *Rec. Trav. chim.*, 1927, **46**, 622).

It appeared desirable therefore to make a further study of the mode of action of hydrogen peroxide in acetic acid solution on oleic and elaidic acids and their methyl esters. Under conditions similar to those described by Hilditch (*loc. cit.*), but with a smaller excess of hydrogen peroxide, there were readily isolated elaidic acid epoxide, m. p. 55·5° (in 25—30% yield from the products of oxidation of elaidic acid), 10—15% of free dihydroxystearic acid, m. p. 132°, and about 50% of its monoacetyl derivatives. Oleic acid, however, afforded no epoxide, the main product being a mixture of monoacetyl derivatives of the dihydroxy-acid, m. p. 95°. Small amounts (not exceeding 2%) of peroxides, probably of the bis-type, CHR(OH)·O·O·CHR·OH (King, J., 1942, 218), were also formed. Similar results were obtained with the methyl esters of oleic and elaidic acids.

Oleic acid epoxide, m. p. 59·5°, united relatively easily with acetic acid, yielding a mixture of monoacetyl derivatives of the dihydroxystearic acid, m. p. 95°, but elaidic acid epoxide was transformed much more slowly into the monoacetyl derivatives of the dihydroxy-acid, m. p. 132°, about 50% remaining unchanged after 11 days at room temperature. It seems reasonable to suppose, therefore, that the reactions take the following course (cf. Böeseken, *loc. cit.*; Böeseken and Elsen, *Rec. Trav. chim.*, 1929, **48**, 363) :

$$\mathrm{R{\cdot}CH{:}CHR' \xrightarrow{AcO_3H} R{\cdot}CH\!-\!CHR' \xrightarrow{AcOH} R{\cdot}CH(OAc){\cdot}CH(OH)R' \text{ and } R{\cdot}CH(OH){\cdot}CH(OAc)R' \xrightarrow{H_2O} R{\cdot}CH(OH){\cdot}CH(OH)R'}$$

Dorée and Pepper (J., 1942, 478) have shown that, when oxidised at 60° by hydrogen peroxide in acetic acid solution in the presence of osmium tetroxide, oleic acid gives the dihydroxy-acid of higher m. p., and elaidic that of lower m. p., but no epoxides were isolated. This accords with the mechanism suggested by Böeseken (*ibid.*, 1922, **41**, 199), postulating the formation of intermediate cyclic osmium compounds (to the exclusion of the usual epoxides) which oppose inversion. The balance of evidence, therefore, contributes further support for the configurational relationships between the unsaturated acids, the oxido- and dihydroxy-stearic acids suggested in a previous communication (J., 1942, 388), and leads with moderate certainty to the following conclusions : (1) Fission of the oxide ring, whether effected by hydrolysis or by union with an acid, is accom-

panied by an inversion of configuration. (2) The conversion of oleic acid by means of cold alkaline permanganate into the dihydroxy-acid of higher m. p. (and of elaidic acid into the dihydroxy-acid of lower m. p.) represents the normal *cis*-addition of two hydroxyl groups to the double bond.

Experimental.

Oxidation of Oleic Acid by Hydrogen Peroxide in Acetic Acid.—A 7% solution of crude oleic acid in acetone deposited saturated acids at −25° and oleic acid at −60° (cf. Brown and Shinowara, *J. Amer. Chem. Soc.*, 1937, **59**, 6). After recrystallisation, saturated acids were removed from a 10% solution at −30°. A solution of hydrogen peroxide (8 ml. of 100-vol.) and oleic acid (10 g., m. p. 7°. Found: I val., 86·6; equiv., 278. Calc. for $C_{18}H_{34}O_2$: I val., 90·1; equiv., 282) in acetic acid (200 ml.) was kept at room temperature for 12 days and then for 48 hours at 0° after addition of water. The dried, sticky product was dissolved in warm benzene (50 ml.), filtered from traces of dihydroxystearic acid, and cooled to 6°. The 9 : 10-hydroxyacetoxystearic acids deposited (5·5 g.) crystallised from acetone in colourless needles, m. p. 81° [Found: C, 66·5; H, 10·7; equiv., 360; sap. val. (excluding acid val.), 156. Calc. for $C_{20}H_{38}O_5$: C, 67·0; H, 10·7%; equiv., 358; sap. val., 156], sparingly soluble in light petroleum, but readily in 2N-sodium hydroxide (distinction from oxidostearic acids). Saponification of this product afforded dihydroxystearic acid, m. p. 94° alone or mixed with an authentic specimen. The benzene mother-liquor contained a small amount of peroxides, and no oxidostearic acid could be isolated.

Oxidation of Elaidic Acid.—A solution of elaidic acid (20 g., m. p. 44·5°. Found: I val., 88; equiv., 281) and hydrogen peroxide (16 ml. of 100 vol.) in acetic acid (400 ml.) was kept for 6 days at room temperature, and water then added. Extraction of the dried product with warm light petroleum (150 ml.) left an insoluble residue of dihydroxystearic acid, which crystallised from alcohol in rhombic plates (2·35 g.), m. p. 131° (Found: C, 68·5; H, 11·6; equiv., 312. Calc. for $C_{18}H_{36}O_4$: C, 68·3; H, 11·4%; equiv., 316). The petroleum extract, concentrated and cooled to 0°, deposited 9 : 10-oxidostearic acid, which separated from acetone in typical rhombic plates (5·5 g.), m. p. 55·5°, alone or mixed with an authentic specimen prepared from dihydroxystearic acid, m. p. 95°, *via* the chlorohydrins (J., 1942, 390) (Found: C, 72·3; H, 11·4; equiv., 296. Calc. for $C_{18}H_{34}O_3$: C, 72·4; H, 11·5%; equiv., 298).

The mother-liquors from the epoxide yielded a clear, viscous oil (7·9 g.), sparingly soluble in light petroleum, consisting of 9 : 10-hydroxyacetoxystearic acids (with a small quantity of peroxides), which slowly set to a crystalline mass, m. p. 40—42°, when kept in a refrigerator [Found: C, 67·4; H, 10·7%; equiv., 359; *M* (Rast), 384; sap. val. (excluding acid val.), 137; active oxygen (Lea, "Rancidity in Edible Fats," 1938, p. 107), 0·124%]. On saponification this furnished a nearly theoretical yield of dihydroxystearic acid, m. p. and mixed m. p. 131°.

Oxidation of Methyl Oleate.—A solution of hydrogen peroxide (6 ml. of 100-vol.) and methyl oleate (10 g., b. p. 226—227°/31 mm. Found: sap. val., 189; I val., 86. Calc. for $C_{19}H_{36}O_2$: sap. val., 189; I val., 86) in acetic acid (100 ml.) was kept for 6 days at room temperature, and then diluted with water. The oil was saponified with 0·6N-alcoholic potassium hydroxide (150 ml.) (19 hours at room temperature), and the solid product obtained on acidification was dried, and extracted with warm light petroleum (180 ml.), leaving an insoluble residue of dihydroxystearic acid (5·7 g.), m. p. 94° alone or mixed with an authentic specimen (Found: C, 68·4; H, 11·4%; equiv., 315).

The petroleum extract left on evaporation a pale yellow oil (1·87 g.), gradually becoming semi-crystalline, and corresponding closely to oxidostearic acid in composition [Found: C, 72·45; H, 11·5%; equiv., 312·5; *M* (Rast), 307; I val., 13·2; active oxygen, 0·02%]. No oleic acid epoxide could, however, be isolated, and no dihydroxystearic acid was obtained after saponification.

Oxidation of Methyl Elaidate.—Methyl elaidate (10 g., b. p. 218—220°/24 mm. Found: I val., 84·5; sap. val., 187) was oxidised for 6 days as described for the oleate. The acids obtained after cold saponification of the product were resolved by extraction with warm light petroleum into an insoluble fraction (7·2 g.), consisting of dihydroxystearic acid, m. p. and mixed m. p. 131° (Found: C, 68·5; H, 11·6%), and a more soluble fraction (2·2 g.) of 9 : 10-oxidostearic acid, m. p. 55·5° alone or mixed with authentic elaidic acid epoxide (Found: equiv., 298·5).

r-9 : 10-*Oxidostearic Acid, m. p.* 59·5° (*Oleic Acid Epoxide*).—Oleic acid epoxide was prepared from dihydroxystearic acid, m. p. 132°, *via* the chlorohydrins (King, *loc. cit.*), and also by the following methods.

(*a*) From oleic acid *via* the chlorohydrins (cf. Ellis, *Biochem. J.*, 1936, **30**, 757). A solution of oleic acid (10 g.) in 1·2N-Liquor Sodæ Chlorinatæ (60 ml.) and water (300 ml.) was made faintly turbid with hydrochloric acid, and then saturated with carbon dioxide. After 18 hours, acidification of the mixture and extraction with ether furnished the chlorohydrins as a clear viscous oil. This was refluxed for 2 hours with 2N-alcoholic potassium hydroxide (200 ml.), and the diluted and acidified solution was cooled in the refrigerator. The dried product was crystallised successively from light petroleum and acetone, yielding oxidostearic acid (3·0 g.) in long, slender laminæ, m. p. alone or mixed with a specimen prepared as above 59·5° (Found: C, 72·5; H, 11·5%; equiv., 298).

(*b*) From oleic acid *via* the bromohydrins. Bromine (1·8 ml.) in 10% aqueous potassium bromide (100 ml.) was added slowly and with vigorous shaking to oleic acid (10 g.) emulsified with water (500 ml.), any excess of halogen being finally removed with aqueous sodium hydrogen sulphite (Read and Reid, J., 1928, 749, 1487). Ether extraction yielded an oily mixture of bromohydrins, which after saponification gave oxidostearic acid (1·4 g.), m. p. and mixed m. p. 59·5°.

Action of Acetic Acid on the Oxidostearic Acids.—(*a*) A solution of oleic acid epoxide (1 g., m. p. 59·5°) in acetic acid (25 ml.) was kept for 7 days at room temperature, then diluted with water and cooled at 0° for 24 hours. The hydroxyacetoxystearic acids crystallised from benzene–alcohol in colourless needles (0·7 g.), m. p. 80·5° alone or mixed with a specimen prepared from oleic acid as above [Found: equiv., 357; sap. val. (excluding acid val.), 157·5]. Saponification afforded dihydroxystearic acid, m. p. 95°, in nearly theoretical yield. No unchanged epoxide was isolated.

(*b*) A solution of elaidic acid epoxide (1 g., m. p. 55·5°) in acetic acid (15 ml.), after 11 days at room temperature, gave unchanged epoxide (0·48 g.) and a colourless oil (0·57 g.). The latter gradually set to a crystalline mass, m. p. 37—39°, sparingly soluble in light petroleum, consisting of crude hydroxyacetoxystearic acids (Found: equiv., 379; sap. val., 149). It afforded a good yield of dihydroxystearic acid, m. p. 131°, on saponification, but could not be purified.

Action of Acetic Acid on the Dihydroxystearic Acids, m. p.'s 95° *and* 132°.—Solutions of the dihydroxy-acids in cold acetic acid were set aside for 14 days. More than 97% of the acids were recovered unchanged, and there was no evidence of epoxide formation.

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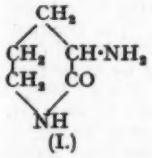
13. *The Anhydrides of Basic Amino-acids.*

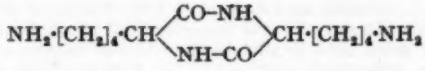
By Donald W. Adamson.

" *dl*-Lysine anhydride " (the product obtained by heating *dl*-lysine methyl ester), which has hitherto been regarded as a substituted diketopiperazine, is now shown to contain at least 40% of dl-3-*aminohomopiperidone*. Similarly, l-3-*aminopyrrolidone* is obtained in good yield by heating the methyl ester of *d*-αγ-diamino-*n*-butyric acid. Some derivatives of these bases are described.

α-Amino-esters are normally converted by heat into the corresponding substituted diketopiperazines, as first observed by Curtius (*Ber.*, 1904, **37**, 1284) for glycine ester. *dl*-Ornithine, however, did not react in this manner, since intramolecular cyclisation to *dl*-3-aminopiperidone (I) occurred even during attempted esterification (Fischer and Zemplen, *Ber.*, 1909, **42**, 4878). The same tendency to cyclisation has been observed with various derivatives of ornithine (Fischer and Bergmann, *Annalen*, 1913, **398**, 115; Thomas, Kapfhammer, and Flaschenträger, *Z. physiol. Chem.*, 1922, **124**, 75).



(I.)



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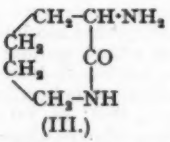

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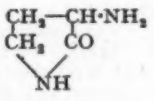

(IV.)

On the other hand, " *dl*-lysine anhydride," obtained as a brown, viscous mass by heating *dl*-lysine methyl ester to 100°, was stated to have the diketopiperazine structure (II) (Fischer and Suzuki, *Chem. Zentr.*, 1905, I, 354; *Ber.*, 1905, **38**, 4173). On repeating this preparation, it is now found that the crude anhydride contains 40% of a white crystalline compound (b. p. 167°/12 mm., m. p. 68—71°) which must be identified as the unimolecular anhydride, dl-3-*aminohomopiperidone* (III), by reason of its volatility. The *picrate* and the *hydrochloride* prepared from this compound are similar to those isolated by Fischer and Suzuki (*loc. cit.*), and it is therefore concluded that their crude anhydride consisted of (III) admixed with non-volatile lysyl peptides.

dl-3-Aminohomopiperidone is strongly basic and hygroscopic and is readily hydrolysed to *dl*-lysine hydrochloride by hydrochloric acid. Acetylation with acetic anhydride under mild conditions yields 3-acetamidohomopiperidone, which had been obtained by Wrede (*Z. physiol. Chem.*, 1932, **206**, 146) by hydrolysis of the base $C_{10}H_{14}O_2N_2$, isolated from the acetylation product of certain proteins, or by acetylation of *d*-lysine under vigorous conditions.

The free amino-group of (III), available for coupling, corresponds to the α-amino-group of the parent lysine (the point of linkage in natural products), whereas the ε-amino-group is protected. Accordingly, (III) condensed with *p*-acetamidobenzenesulphonyl chloride to give dl-3-(p-*acetamidobenzenesulphonamido*)*homopiperidone*, which was hydrolysed to *ε-amino-α-*(p-*aminobenzenesulphonamido*)-n-*hexoic acid*. It is also possible that (III) may serve for the synthesis of lysyl peptides (compare Bergmann and Koster, *Z. physiol. Chem.*, 1927, **167**, 91, who report that the lactam group of 3-acetylphenylalanylaminopiperidone may be hydrolysed, leaving the peptide link intact).

As expected, methyl *d*-αγ-diamino-*n*-butyrate (available from glutamic acid; Adamson, J., 1939, 1564) was readily converted into l-3-*aminopyrrolidone* (IV). The preparation of the *picrate* and the *hydrochloride* of this base and of 3-*acetamido*- and 3-(p-*acetamidobenzenesulphonamido*)-*pyrrolidone* is described.

Experimental.

dl-*Lysine Methyl Ester Dihydrochloride*.—Methyl alcohol (340 c.c.) containing a suspension of *dl*-lysine dihydrochloride (17·0 g.) (Adamson, *loc. cit.*) was saturated with dry hydrogen chloride without cooling. Crystallisation of the hot, clear solution commenced on cooling, and was completed by addition of ether (340 c.c.). After standing overnight, the precipitate was filtered off, washed with methyl alcohol–ether, and dried in a vacuum. Yield, 17·5 g. (98%); m. p. 217—218° (Fischer and Suzuki, *loc. cit.*, give m. p. 218°).

" dl-*Lysine Anhydride*."—Sodium (2 g.) was dissolved in methyl alcohol (100 c.c.) and added to a solution of *dl*-lysine methyl ester dihydrochloride (10 g.) in warm methyl alcohol (100 c.c.). Ether (500 c.c.) was added, and the mixture kept for several hours. Sodium chloride was then removed, and the filtrate evaporated under reduced pressure; the residual gum was heated at 100° for 2 hours. The product (5·3 g.) was a pale brown, viscous mass which partly solidified when kept at 0° for several days (compare Fischer and Suzuki, *loc. cit.*).

dl-3-*Aminohomopiperidone*.—" *dl*-Lysine anhydride " (10 g., prepared as above) was distilled from an oil-bath under reduced pressure. The volatile fraction (3·9 g.), collected at 165—167°/12 mm., solidified on cooling (m. p. 60—63°); redistillation gave long white needles, b. p. 167°/12 mm., m. p. 68—71° (Found: C, 56·4; H, 9·6; N, 21·9. $C_6H_{12}ON_2$ requires C, 56·3; H, 9·4; N, 21·9%). The *base* was soluble in water, sparingly soluble in alcohol, and insoluble in other organic solvents. The distillation residue (*ca.* 6 g.) was a dark brown resin, insoluble in hot water and organic solvents.

Hydrolysis. The base (0·11 g.), dissolved in hydrochloric acid (20%, 3 c.c.), was heated on the water-bath for 1 hour, and the product evaporated to dryness. The residue was dissolved in a little water, and picric acid (0·5 g.) in water (40 c.c.) added; *dl*-lysine dipicrate which separated had m. p. 186—188°, not depressed by admixture with an authentic specimen (Adamson, *loc. cit.*).

Hydrochloride. Dry hydrogen chloride was passed into a solution of the base (0·26 g.) in methyl alcohol (5 c.c.), and the white crystalline *hydrochloride* which separated was filtered off, washed with ether, and dried in a vacuum; m. p. 294—296° (decomp.) (Found: N, 16·5; Cl, 21·2. $C_6H_{13}ON_2Cl$ requires N, 17·0; Cl, 21·6%). Data for the " *dl*-lysine anhydride dihydrochloride " of Fischer and Suzuki (*loc. cit.*) are recorded variously as " m. p. 270° "; " colours at 225°, then sinters and melts at a higher temperature with frothing."

Picrate. Picric acid (0·3 g.) in water (30 c.c.) was added to a solution of the base (0·17 g.) in water (5 c.c.) and set aside for 24 hours. Recrystallisation of the resulting precipitate (0·33 g.) from a little hot water gave long needles of the *picrate*; it darkened at 215°, m. p. 233° (decomp.) (Found: N, 19·8. $C_6H_{12}ON_2,C_6H_3O_7N_3$ requires N, 19·6%). According to Fischer and Suzuki, "*dl*-lysine anhydride dipicrate" darkens at 210°, m. p. 230° (decomp.).

dl-3-*Acetamidohomopiperidone.*—The base (0·5 g.) was dissolved in acetic anhydride (1·2 g.) and heated at 100° for 5 mins., excess of the anhydride then being removed by several evaporations with 5 c.c. portions of ethyl alcohol. The solid residue was obtained as clusters of white needles, m. p. 162°, by recrystallisation from acetone (Found: C, 56·4; H, 8·2; N, 16·3. Calc. for $C_8H_{14}O_2N_2$: C, 56·5; H, 8·2; N, 16·5%) (Wrede, *loc. cit.*, gives m. p. 163°).

3-(p-*Acetamidobenzenesulphonamido*)*homopiperidone.*—The base (1·65 g.) in chloroform (10 c.c.) was added to *p*-acetamidobenzenesulphonyl chloride (3·1 g.) in chloroform (35 c.c.). The crystalline precipitate was washed with boiling water (50 c.c.) and recrystallised from a large volume of alcohol. Yield, 1·85 g., m. p. 286—288° (decomp.) (Found: C, 52·0; H, 5·9; N, 12·8; S, 9·8. $C_{14}H_{19}O_4N_3S$ requires C, 51·7; H, 5·9; N, 12·9; S, 9·8%). A solution of 1·5 g. of this *compound* in hydrochloric acid (12%, 10 c.c.) was refluxed for 2 hours. After neutralisation with ammonia, the solution was cooled to 0° for 2 days, whereupon small prisms of *ε-amino-α-*(p-*aminobenzenesulphonamido*)-n-*hexoic acid* (0·85 g.) separated; recrystallised from a small volume of aqueous alcohol, these had m. p. 286° (decomp.) (Found: N, 13·9; S, 11·1. $C_{12}H_{19}O_4N_3S$ requires N, 14·0; S, 10·6%).

1-3-*Aminopyrrolidone.*—A suspension of *d-αγ*-diamino-*n*-butyric acid dihydrochloride (25 g.) (Adamson, *loc. cit.*) in methyl alcohol (750 c.c.) was saturated with dry hydrogen chloride without cooling. After refluxing for 6 hours, the methyl alcohol and hydrogen chloride were removed by evaporation under reduced pressure at 30°. The residual gum (26·3 g.) was dissolved in hot methyl alcohol (50 c.c.), cooled, and sodium (6·1 g.) dissolved in methyl alcohol (200 c.c.) added. Ether (700 c.c.) was added, sodium chloride filtered off, and the ether and alcohol removed by evaporation at 30°. The solid residue was heated at 100° for 40 mins. and finally distilled, 1-3-*aminopyrrolidone* (8·9 g., 68% yield) being collected at 175°/20 mm.; white needles, m. p. 106—108°, $[\alpha]_D^{18°}$ −31·7° (*c*, 6·69 in water) (Found: C, 48·4; H, 7·8; N, 28·0. $C_4H_8ON_2$ requires C, 48·0; H, 8·0; N, 28·0%). The base quickly absorbs carbon dioxide from the air, is very soluble in water, moderately soluble in alcohol and chloroform, and only sparingly soluble in ether and light petroleum. Hydrolysis with hydrochloric acid gave *d-αγ*-diamino-*n*-butyric acid dihydrochloride, m. p. 193—195°, characterised by conversion into the dipicrate, m. p. 188° (Adamson, *loc. cit.*).

The *hydrochloride* was precipitated as fine white crystals when hydrogen chloride was passed into a solution of the base in alcohol; m. p. 198—200° (Found: N, 20·1; Cl, 25·7. $C_4H_9ON_2Cl$ requires N, 20·5; Cl, 26·0%). The *picrate*, prepared by mixing picric acid and the base in alcoholic solution, was obtained as prisms by recrystallisation from aqueous alcohol; m. p. 185—187° (darkened at 170°) (Found: N, 21·3. $C_4H_8ON_2,C_6H_3O_7N_3$ requires N, 21·3%). Acetylation by means of acetic anhydride gave 3-*acetamidopyrrolidone*; recrystallised from hot acetone, this had m. p. 176° (Found: C, 50·8; H, 6·8; N, 19·8. $C_6H_{10}O_2N_2$ requires C, 50·7; H, 7·0; N, 19·7%).

3-(p-*Acetamidobenzenesulphonamido*)*pyrrolidone.*—The base (1·5 g.) in hot acetone (20 c.c.) was added to *p*-acetamidobenzenesulphonyl chloride (3·4 g.) in hot acetone (20 c.c.). The solid which separated was filtered off and recrystallised several times from hot water; m. p. 222—224° (decomp.) (Found: C, 48·8; H, 5·2; N, 14·4; S, 11·0. $C_{12}H_{15}O_4N_3S$ requires C, 48·5; H, 5·1; N, 14·1; S, 10·8%). A solution of this *compound* (2·5 g.) in hydrochloric acid (12%, 12 c.c.) was boiled under reflux for 2 hours. The cooled solution was neutralised with ammonia, and the precipitate of *γ-amino-α-*(p-*aminobenzenesulphonamido*)-n-*butyric acid* (2·1 g.) recrystallised from much hot water, m. p. 259—260° (decomp.) (Found: N, 15·4; S, 11·8. $C_{10}H_{15}O_4N_3S$ requires N, 15·4; S, 11·7%).

The author thanks Sir Robert Robinson, F.R.S., and Dr. James Walker for their interest in the work, and I.C.I. (Dyestuffs) Limited for permission to publish the results.

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14. *Some Yttrium-group Oxalates.*

By JOSEPH K. MARSH.

Yttrium oxalate forms 6-, 10-, and 17-hydrates, but the 9-hydrate commonly cited is found to be a complex ammonium salt. Ytterbium oxalate hexahydrate has been prepared.

IN the cerium group of rare earths the oxalate most commonly formed on precipitation is the decahydrate, though a number of others, particularly the 9- and the 11-hydrates, are known. In the yttrium group the results recorded are more diverse, and particulars of conditions of precipitation are usually lacking. A thorough investigation of these entities would involve prolonged phase-rule studies, but it is now found that precipitation of the oxalates under the conditions usual in practice frequently affords definite pure hydrates.

The 6- and 10-*hydrates* of yttrium oxalate have not hitherto been reported, and the 17-hydrate appears to be peculiar to yttrium. 6-, 9-, 10-, 12-, and 14-Hydrates of erbium oxalate have been recorded. The hexa- and the deca-hydrate, which are paralleled by other neighbouring earths, can be accepted with certainty, but owing to the great difficulty of obtaining erbium material free from yttrium, the existence of the higher hydrates is doubtful: they probably result from admixture of the 17-hydrate with the lower hydrates.

The ytterbium oxalate decahydrate described by Nilson (*Ber.*, 1880, **13**, 1430) and by Rimbach and Schubert (*Z. physikal. Chem.*, 1909, **67**, 196) was not obtained. The heptahydrate has been described by Bodlaender (Diss., Berlin, 1915, 14), but the ***hexahydrate***, which appears to be the most stable oxalate, is new.

It would seem that all the rare earths in serial order from lanthanum to erbium or ytterbium yield oxalate decahydrates, and all the earths from yttrium or erbium to lutecium probably yield oxalate hexahydrates.

In precipitating the yttrium earth oxalates the formation of the dense hexahydrate at the boiling point should be aimed at in order to facilitate subsequent ignition to oxide.

EXPERIMENTAL.

A nitrate solution of the earth was mixed with 2N-nitric acid to give a N/2-solution of the earth for experiments at low temperatures, or a N-solution for those at high temperatures. To these mixtures 10% oxalic acid was added very slowly

(1 hour) but in excess, so that precipitation of oxalate was avoided as far as possible, and a slow crystal growth occurred. This was allowed to proceed for 4 hours. Sometimes there was an initial precipitation of oxalate, followed by crystal growth. After the separation of the hydrates from hot solution another small, well-crystallised crop of oxalate was obtained by allowing the mother-liquor to cool overnight. The weighed oxalates were dried at 130° and then ignited in a gas crucible furnace to constant weight of oxide. The oxalate radicals were estimated by titration of weighed samples of the salts with N/10-potassium permanganate.

The yttrium used contained a small quantity of erbium, which was estimated by comparison of the absorption spectrum with a standard erbium solution. The amount found (0·25%) was calculated to raise the effective atomic weight of yttrium to 89·1, and this value has been used in calculating the theoretical composition of the yttrium salts. The erbium material available contained considerable yttrium. Samples of oxalate precipitated at 0° gave Er_2O_3, 44·57; C_2O_4, 33·35%. The formula $Er_2(C_2O_4)_3$ being assumed, the effective atomic weight of erbium is found to be 152·5. This value has been used in computations. The erbium oxalate hydrates must be deduced solely from ignition data. Most of the oxalate determinations were not made till 2 years after those of the oxides.

Dysprosium Oxalate.—The precipitate at 100° was the known decahydrate (Found: Dy_2O_3, 48·74, 48·78; C_2O_4, 34·43. Calc.: Dy_2O_3, 48·50; C_2O_4, 34·34%). This also separated on cooling from 90° to 15°, but the precipitate at 15° appeared to be a hydrate with $11H_2O$, but it lost water on storing [Found: Dy_2O_3, 47·63, 47·58. Calc. for $Dy_2(C_2O_4)_3,11H_2O$: Dy_2O_3, 47·40%].

Yttrium Oxalate.—The precipitate at 100° was a ***hexahydrate***. It formed a dense, hard cake of prismatic crystals [Found: Y_2O_3, 40·05; C_2O_4, 47·83. $Y_2(C_2O_4)_3,6H_2O$ requires Y_2O_3, 40·11; C_2O_4, 47·97%]. The precipitate between 90° and 15° was well crystallised and proved to be the ***decahydrate***. It resembled the decahydrates of dysprosium and gadolinium oxalates [Found: Y_2O_3, 36·40; C_2O_4, 42·45. $Y_2(C_2O_4)_3,10H_2O$ requires Y_2O_3, 36·35; C_2O_4, 42·43%]. The precipitate at 15° was the 17-hydrate described by Brauner (J., 1898, **73**, 951) (Found: Y_2O_3, 29·99, 30·16; C_2O_4, 35·30. Calc.: Y_2O_3, 30·24; C_2O_4, 35·29%). At 0° there was obtained a precipitate corresponding to a 12·4-hydrate, but this was probably not homogeneous.

The nonahydrate has been regarded as the most usual hydrate of yttrium oxalate. In its preparation, Bahr and Bunsen (*Annalen*, 1866, **137**, 1) and Rimbach and Schubert (*Z. physikal. Chem.*, 1909, **67**, 196) used ammonium oxalate as precipitant, but with this reagent the author obtained a precipitate which on ignition yielded an oxide residue corresponding to $Y_2(C_2O_4)_3,8{\cdot}75H_2O$. Washed four times with boiling water, the precipitate continued to give a strong Nessler reaction, and on ignition it liberated a distinct odour of ammonia. It is not therefore a simple yttrium oxalate.

Erbium Oxalate.—The hexahydrate was prepared by precipitation at 100° with oxalic acid. It was similar in appearance to the corresponding yttrium salt [Found: Er_2O_3, 52·10. Calc.: 52·14%]. A small precipitate obtained on cooling (90—15°) resembled the decahydrates of other rare earths, but was not analysed.

Ytterbium Oxalate.—The ***hexahydrate*** was precipitated at 100° [Found: Yb_2O_3, 55·00, 54·87; C_2O_4, 36·51. $Yb_2(C_2O_4)_3,6H_2O$ requires Yb_2O_3, 54·87; C_2O_4, 36·77%]. The heptahydrate was precipitated at 15° (Found: Yb_2O_3, 53·65, 53·67. Calc.: Yb_2O_3, 53·60%); on keeping it formed the hexahydrate.

INORGANIC CHEMISTRY LABORATORIES, SOUTH PARKS ROAD, OXFORD. [*Received, May 23rd*, 1941.]

NOTES.

A Rapid Volumetric Method for the Determination of Lead in Brass. By PHILLIP M. FISK and FRANCIS F. POLLAK.

THE estimation of lead in brass, except for traces, is normally based on its separation by electrolysis or by precipitation as sulphate. Electrolysis, is rendered difficult in the presence of interfering elements, and the sulphate method needs a tedious separation from the matter insoluble in nitric acid. Starting from the impure sulphate, a number of methods have been developed, such as the molybdate and the chromate method, having in common the use of ammonium acetate as a solvent for lead sulphate before the final determination. Direct precipitation as chromate without preliminary separation as the sulphate under conditions described below is, however, more rapid and accurate.

Special Solutions Required.—Nitric acid, 1 : 1 by vol. Potassium dichromate, saturated. Phosphoric–sulphuric acid mixture: 100 ml. of phosphoric acid (*d* 1·75) and 180 ml. of sulphuric acid (*d* 1·8) made up to 1 l. Ferrous ammonium sulphate: 20 g. in 50 ml. of 20% sulphuric acid made up to 1 l. Sodium diphenylaminesulphonate indicator: 0·5 g. of sodium sulphate in 10 ml. of water added to 0·32 g. of the barium salt in 90 ml. of water and filtered.

Method.—For 1—4% of lead, 1·5 g. of drillings are dissolved in 15 ml. of the nitric acid in a 400-ml. conical beaker. The solution is heated to expel nitrous fumes, diluted to 100 ml., cooled, and neutralised with anhydrous sodium carbonate. Glacial acetic acid is added to dissolve the precipitate and then 10 ml. in excess. It may be found more convenient to use ammonia instead of sodium carbonate, but as an excess of ammonium acetate has a distinct solvent action on lead chromate, ammonia should be added until the precipitate first formed just dissolves: about 30 ml. of 5N-ammonia, followed by 15 ml. of glacial acetic acid, is convenient. To the acetic acid solution, 10 ml. of saturated potassium dichromate diluted to 20 ml. are added. After 3 mins.' boiling, the lead chromate becomes orange and dense; on settling, it is filtered off through an 11-cm. No. 41 Whatman filter paper. Beaker and filter are washed free from soluble chromate with hot 5% acetic acid and finally with hot water. The filter-paper containing the precipitate is placed into the original beaker, and 25 ml. of the acid mixture washed down the sides of the beaker. The lead sulphate produced is dissolved on shaking by the addition of 5 g. of solid ammonium chloride. The solution is made up to 120 ml. with cold water. Fragments of filter-paper do not interfere with the subsequent titration. 25 Ml. of ferrous ammonium sulphate solution are added from a pipette, excess being titrated with N/20-potassium dichromate, 3 drops of sodium diphenylaminesulphonate solution being used as indicator, to a purple colour which persists on shaking. The ferrous ammonium sulphate is standardised by using 25 ml. of the solution, 25 ml. of acid mixture, 100 ml. of water, and 3 drops of indicator. The difference in the volumes of dichromate in ml. $\times 0{\cdot}003453$ = weight of lead in g. The dichromate solution is standardised against pure lead, taken through all the foregoing steps. The time for the lead estimation is 30 mins.

Interfering Elements.—Copper, cadmium, zinc, manganese, iron (III), aluminium, nickel, and cobalt do not interfere. Tin, converted into metastannic acid, will occlude alkali chromate, but up to 0·015 g. (*i.e.*, 1% Sn) this is negligible. Therefore, up to 1% of tin it is not necessary to filter off the metastannic acid before precipitation of the chromate. Antimony would give similar results, but it is almost absent in normal brasses and can be ignored. Arsenic yields lead arsenate insoluble in acetic acid, but does not interfere up to 0·0015 g. (*i.e.*, 0·1% As), as lead chromate is produced with excess of the dichromate. Bismuth may be ignored up to 0·1% if an excess of 15 ml. of acetic acid is used. Addition of citric acid before filtration offered no advantage. Phosphorus gives lead phosphate, insoluble in acetic acid, but up to 0·015 g. (*i.e.*, 1% P) the excess of dichromate converts the phosphate into the chromate and in any case most of the phosphorus present will be precipitated with the tin during solution in nitric acid.

A solution of nitrates of the following metals, giving impurities at least 10 times those normally present in commercial brass, gave results far more accurate than those obtained by the sulphate method: Cu, 55·50; Zn, 34·81; Pb, 2·77; Cd, 0·93; Ni, 1·73; Co, 0·84; Mn, 1·71; Fe, 0·86; Al, 0·85% (Found: Pb, by chromate method, 0·0485, 0·0487, 0·0487 g.; by sulphate method, 0·0479, 0·0478, 0·0480 g. Taken: Pb, 0·0486 g.).

Our thanks are due to the Directors of the Crittall Manufacturing Co. for permission to publish this method, and to Mr. Wellburn of the Plessey Co., Ilford, for critical examination of the method.—[*Received, October 5th*, 1942.]

Some Notes on the Condensation Products of Acetaldehyde. By Ernest E. Connolly.

Aldol.—It is well known that the condensation of acetaldehyde under the action of alkaline catalysts yields aldol. This is usually described (*e.g.*, Heilbron, "Dictionary of Organic Chemistry") as a viscous liquid, $d^{18°}$ 1·11, but it is doubtful if this is true acetaldol. The normal product of the condensation of acetaldehyde at room temperature, with a catalyst such as sodium hydroxide, is a colourless, somewhat syrupy liquid, $d^{20°}$ *ca.* 1·06. This "crude aldol" contains some 35% by weight of recoverable acetaldehyde. Further condensation, with increase of density to about 1·11, may be effected by stirring the crude aldol with 0·5% of calcium hydroxide; the product is miscible with water, but on distillation with dilute mineral acid it yields no more crotonaldehyde than the original crude aldol, but only enhanced quantities of higher-boiling unsaturated aldehydes, amongst which have been identified two hexadienals and one octatrienal. On reduction, these yield primary higher alcohols found in the crude butanol from the hydrogenation of technical crotonaldehyde. The aldol condensation products studied by Plant (J., 1938, 536) are probably of this nature.

Of the recoverable aldehyde present in crude aldol, only about one-half is readily removed at room temperature by a current of inert gas or application of vacuum. The remaining half appears to be set free very slowly and is possibly present as the "semiacetal" postulated by Shilov (*J. Appl. Chem. U.S.S.R.*, 1935, **8**, 93). Substantially the whole of the unreacted aldehyde may, however, be removed by distillation with benzene or by passing the neutralised crude aldol through a tube at 100°. The residual product in both cases, however, crystallises as paraldol.

By the vacuum fractionation of crude aldol or paraldol there is obtained a colourless mobile liquid, b. p. 75°/16 mm., $d^{20°}$ 1·01. This quickly starts to polymerise, with evolution of heat, giving "viscid aldol" and finally crystalline paraldol. The change is accelerated by traces of electrolytes and this presumably unimolecular aldol cannot be stabilised by addition of pyridine, quinol, or resorcinol. It appears, however, to be fairly stable at −80°.

The rapid polymerisation of the mobile aldol makes it difficult to determine its properties, but by working as quickly as possible, the following results were obtained: $d^{20°}$ 1·009, n_D 1·4280, whence $[R_L]_D$ 22·44, indicating coupling through one oxygen atom; *M* (cryoscopic in benzene), 88, 89. Viscid and mobile aldol have been mentioned by Nowak (*Monatsh.*, 1901, **22**, 1140); the former is probably chiefly supercooled paraldol.

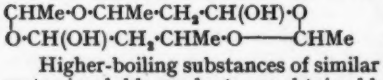
Paraldol.—The molecular weight of crystalline paraldol (cryoscopic in benzene) was found to be 175, 175. In the supercooled liquid state it showed $d^{20°}$ 1·116, $n_D^{20°}$ 1·4610, giving $[R_L]_D$ 43·26. If we take $[R_L]_D$ for aldehyde as 11·51, the fall in refraction in passing to paraldol is 4 × 0·69, indicating a coupling through all the oxygen atoms present. Paraldol is therefore probably cyclic, like paraldehyde, and it is possible also that there is an aldol–paraldol equilibrium.

By the hydroxylamine salt method paraldol is titrated quantitatively as aldol, and by fractionation from dilute acid it yields crotonaldehyde quantitatively.

Higher Condensation Products.—A condensation product not hitherto described is obtained by stirring crude aldol with 2% of sulphuric acid for some hours, followed by neutralisation, water washing, and vacuum fractionation. It is a colourless, viscid liquid, b. p. 136°/17 mm., nearly insoluble in water: $d^{20°}$ 1·063, $n_D^{20°}$ 1·442; *M* (cryoscopic in benzene), 245, 247.

With aqueous or alcoholic hydroxylamine hydrochloride, there was only a small immediate reaction, probably due to a little aldol still present. After overnight standing, however, titration showed 1 c.c. of N-sodium hydroxide = 0·0629 g. of the substance. Distillation from dilute sulphuric acid, and collection in ice-water gave a similar total figure for the titration of the distillate: 1 c.c. of N-alkali = 0·0651 g. Analysis of the distillate and calculation back to *M* 246 showed that 1 mol. gave 1·95 mols. of acetaldehyde and 1·92 mols. of crotonaldehyde. The production of acetaldehyde and crotonaldehyde in equimolecular proportion was confirmed on a 100-g. sample by fractional distillation.

The substance shows no immediate reaction with aqueous bromine. It is suggested tentatively that it is a doubled form of Shilov's "cyclic semi-acetal," *i.e.*, as inset. With the vacuum-distillation facilities available, slight decomposition during distillation could not be avoided, so a high degree of purity could not be attained. The liquid also showed no signs of crystallising down to −80°.



Higher-boiling substances of similar character are present in the viscous distillation residue. Similar, almost resinous, water-insoluble products are obtained by long storage of slightly acid crude aldol in a vacuum.

The author thanks the directors of British Industrial Solvents Ltd. for permission to publish this note.—[*Received, September 24th*, 1942.]

OBITUARY NOTICES.

MATTHEW HUNTER.

1863—1941.

DR. MATTHEW HUNTER, C.I.E., was born near Settle in 1863 and went to Giggleswick school. From that school he obtained a scholarship in Natural Sciences at Queen's College, Oxford, where he took the Final Honours School in Natural Science. He was awarded the Burdett Coutts University Scholarship in geology and studied later at the Universities of Strasburg and Heidelberg.

In 1890 Hunter entered the service of the Educational Syndicate, Rangoon, a body which, at that time, controlled education in Burma, as a lecturer in Rangoon College. The College was affiliated to the University of Calcutta and remained so until the foundation in 1920 of the University of Rangoon. Hunter remained on the staff of the College until his retirement in 1923. He served first as senior lecturer in Chemistry, then as Professor of Chemistry and finally, after several times officiating in the appointment, as Principal of the College. He also acted for a number of years as Chemical Examiner to the Government of Burma. In 1904 he was appointed to the Indian Educational Service. In 1916 he was awarded the C.I.E.

The last Burmese war had only just ended when Hunter went to Burma and the next thirty years saw great changes. Amongst these was a great increase in the number of Burmans employed in Government service. Many of them were Hunter's old pupils. He never forgot a face and a journey with him in Burma was enlivened by a constant stream of reminiscences. At every railway station old pupils would come to pay their respects and his recollection of their names and college careers was instant and accurate. Many of them had spent college vacations with him, walking in the hills of the Shan plateau before ever the railway from Thazi was made. Many also owed their college careers to his generosity, which was as unfailing as it was spontaneous. He was deservedly respected by his old pupils and returned their affection. Probably the saddest moment of his career in Burma was when, in 1920, at the time of the first College strike, he failed to persuade his students to return. This estrangement was temporary, and when he left Burma in 1923 many hundreds of past and present students came to the jetty to pay their respects to their old teacher.

Hunter was slow to form his judgments but tenacious in holding them. He did not take kindly to Committee government. His treatment of his College Council rather resembled that attributed to Lincoln in his dealings with his Cabinet. He was a shrewd and kindly judge of character, patient and exceptionally helpful to beginners. The author owed much to his advice and help.

During Hunter's service in Burma Rangoon College grew from a small institution, affiliated to Calcutta University and with only a few score pupils, to a great college with over a thousand students and, under the title of University College which was bestowed upon it, the chief unit of the University of Rangoon. In 1915 the new Chemistry wing, designed by Hunter, was opened for use. Before he left he saw the site acquired and plans prepared for what was to become one of the largest residential Universities in Asia. In 1922 the University of Rangoon awarded him the degree of Doctor of Science, *honoris causa*.

Hunter took great interest in the athletic life of the College and built up an Association football team which was for long unbeaten. For many years he acted as Secretary and Treasurer to the Rangoon Literary Society, which, founded in 1857, was for long the chief general Library not only for Rangoon but also for the whole of Burma. It was an arduous task which he discharged with great zeal until his retirement in 1923.

Hunter joined the Chemical Society in December, 1885, and was one of the small band of Fellows whose membership lasted for over fifty years. He died in May, 1941.

D. H. PEACOCK.

WALTER ODLING.

1852—1942.

WALTER ODLING was born on April 14th, 1852. He was the son of a surgeon and was educated at the City of London School, where he took the Edkin Memorial medal for mathematics and gained the medal for chemistry. He also obtained the Mortimer Exhibition for chemistry and a Whitworth Scholarship for science. Through the advice and influence of his cousin, Dr. William Odling, F.R.S., he went to the Royal College of Chemistry and School of Mines, and later became private assistant to Sir Edward Frankland, F.R.S. He was elected a Fellow of the Chemical Society in 1873 and in 1885 became one of the first Fellows of the Institute of Chemistry. In 1935 the Institute awarded him the Frankland medal. In 1874, he was appointed Chemist and Brewer to Messrs. Bass and Co., Burton-on-Trent, by the late John Gretton. He was there nearly 50 years and was Head Brewer at the Old Brewary for 28 years, retiring at the age of 70 in 1922.

Odling was one of the founders of the Burton Archæological Society and for 12 years Chairman of the School of Science.

He married first a sister of Dr. Horace Brown, F.R.S., a Director of Messrs. Worthington, Brewers, and Professor Adrian I. Brown, F.R.S., Professor of Brewing at the Birmingham University. In 1904, he married Lydia Mary, daughter of George Lloyd Williams.

Odling came of a long-lived family. His grandfather, Charles Odling of Tetney, Lincolnshire, was born in 1750 in the reign of George II and his father was born in 1793 in the reign of George III.

G. LLOYD WILLIAMS.

REECE HENRY VALLANCE.

1888—1942.

REECE HENRY VALLANCE died at Birmingham, after a brief illness, on September 27th, 1942, in his 55th year. He was born at Tamworth and educated at the local Grammar School; after matriculating at London University, he continued his studies at the Municipal Technical School, Birmingham, now the Central Technical College, and at Birmingham University, where he graduated B.Sc. in 1910. On the outbreak of war in 1914, he enlisted in the 17th Royal Warwickshire Regiment and, because of his scientific knowledge, was transferred in the following year to the special Brigade, R.E. He fought at Loos, Hullach, Cuinchy and on the Somme and was seriously wounded at Beaumont Hamel in June, 1916. This led to his being invalided out of the army in the autumn of 1917, and he was then appointed chemistry master at King's Norton Secondary School, Birmingham. Two years later he was appointed lecturer in the Chemistry Department of the Municipal Technical School, a position which he occupied until his death. He continued his research work and in 1922 was awarded the M.Sc. In 1918 he had been elected an associate of the Institute of Chemistry, and in 1927 he received the Fellowship. In 1931 he became a Fellow of this Society and contributed several valuable papers to the *Journal*.

He was author of " Arsenic," joint author with D. F. Twiss and (Miss) A. R. Russell of " Sulphur, Selenium and Tellurium " and with A. A. Eldridge of " Chromium and its Congeners," Vols. IV. (Part 4) and VII. (Parts 2 and 3) respectively of "A Textbook of Inorganic Chemistry " edited by J. Newton Friend.

In his researches Vallance covered a wide field, including studies of Caro's peroxymonosulphuric acid, adsorption, iron carbonyl, and determinations of the solubilities of ferrocyanides. Perhaps his most valuable work was on complex acid tungstates and sodium paratungstate. Papers on all of these subjects are published in the *Journal*.

Vallance was extremely popular with his colleagues and students. His serene, unruffled temper and his desire to help made him much beloved by all. He was much more than a brilliant chemist; he studied the humanities as well. He will long be remembered both at home and at College for his welfare activities. He was Chairman of the Hampton in Arden Scout Group Committee. He was also a Gas Identification Officer and frequently lectured on Home Defence.

He is survived by his wife and two children—a son, serving his country in the Navy, and a daughter, serving as a nurse in S. Africa.

J. NEWTON FRIEND.

WILLIAM JOHN YOUNG.

1878—1942.

ON January 26th, 1878, William John Young was born in Manchester, England. In childhood he early showed an interest in science, and after leaving school entered Owens College, Manchester, eventually graduating as Master of Science. Later he obtained the coveted Doctor of Science, London.

In 1902, Young commenced research work at the Lister Institute and was associated with the famous biochemist Harden. The first important discovery made by these two investigators was of the significance of phosphate in yeast juice fermentation. If yeast juice be allowed to ferment sugar, the rate of carbon dioxide evolution is at first rapid but gradually diminishes. If, now, alkali phosphate be added, the evolution of carbon dioxide is immediately increased. Presently the production of gas lessens, to be stimulated once more by further addition of phosphate. Phosphate ions disappear and organically bound phosphates temporarily take their place. Harden and Young found that the formation of phosphoric esters was an integral part of the conversion of sugar into alcohol. Of great theoretical and practical interest was their further observation that, if the yeast juice were dialysed, a colloidal enzyme fraction was retained by the dialysing membrane and this had no longer any powers of fermentation. When the diffusible thermostable component of the juice was added to the thermolabile non-diffusible portion, fermentation readily occurred.

Later work confirmed their investigations and now it is realised that in yeast dialysate there are at least three phosphorus compounds necessary for enzyme activity in fermentation; these are aneurin pyrophosphate (vitamin B_1 pyrophosphate), co-enzyme I (a dinucleotide), and adenyl pyrophosphate. These discoveries of Harden and Young were an introduction to a variety of interesting researches by many workers which revealed the importance of phosphorus in cellular metabolism. The modern interpretation of the chemistry of muscular contraction is a further development of the work initiated by them.

When the Australian Institute of Tropical Medicine was founded in Townsville, Young was appointed to the post of biochemist and with his wife and daughter—now Dr. Sylvia Young of the Department of Public Health, Jerusalem—spent several happy years in this North Australia setting. In 1919, Professor W. A. Osborne was instrumental in obtaining the appointment of Young as lecturer in biochemistry in Melbourne in succession to the late A. C. H. Rothera. It was then that the writer first met Young and for more than twenty years was closely associated with him in the teaching of biochemistry in the University of Melbourne. He later became Professor of Biochemistry and developed a very sound school in that subject. In all these years Young was an indefatigable worker and ever-delightful associate. He was deeply interested in the applied aspects of biochemistry and conducted researches in the ripening of fruits, especially bananas, and also in the problems associated with the transport of meat. As a member of the National Nutrition Committee and a consultant to the Council for Scientific and Industrial Research he contributed much useful, practical advice.

Young was very fond of walking in the country and for many years was a member of a well-known walking club in Melbourne. His familiar figure was invariably present at the fortnightly outings. He was a charming companion and a welcome visitor everywhere, for he was always interested in the affairs of others and had the extraordinary and most endearing faculty of remembering any trivial happenings in the lives of his very large circle of friends who mourn his untimely passing.

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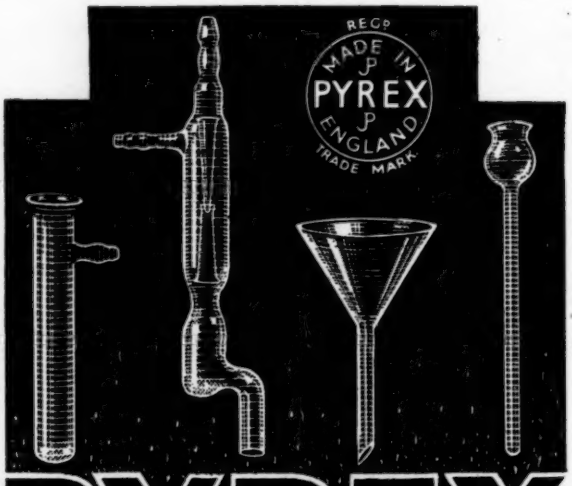

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